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The Mechanism of Cerium (IV) Oxidations of Cyclic Alcohols

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THE MECHANISM OF CERIUM(IV) OXIDATIONS OF CYCLIC ALCOHOLS

A thesis submitted by

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SUMMARY

The mechanisms of cerium(IV) oxidations of a series of cyclic alcohols and glycols were studied in 1.0M perchloric acid and in mixed sulfuric and perchloric acids.

In the reactions of cis- and trans-1,2-cyclohexanediols, trans-2-methoxycyclohexanol, and cyclohexanol in 1.0M perchloric acid at 15.0°C. definite evidence was obtained for complex formation. Apparent formation constants determined by Duke's kinetic and Ardon's spectrophotometric techniques agreed reasonably well. Values obtained from the kinetic data were: cyclohexanol, $2.9\underline{M}^{-1}$; trans-2-methoxycyclohexanol, $2.1\underline{M}^{-1}$; cis-1,2-cyclohexanediol, $29.0\underline{M}^{-1}$; trans-1,2-cyclohexanediol, $18.0\underline{M}^{-1}$. The magnitudes of these equilibrium constants indicate that the 1,2-cyclohexanediols react via chelate complexes.

The reactions of cis- and trans-1,2-cyclopentanediols and trans-2-methoxycyclopentanol were too rapid in 1.0M perchloric acid to be studied by ordinary kinetic procedures. These compounds were therefore studied in mixed sulfuric and perchloric acids. However, positive evidence for complex formation could not be obtained for the reactions in sulfate ion-containing media, although the possibility of complex intermediates could not be ruled out. The energies and entropies of activation for the reactions of these compounds and cyclopentanol, cis- and trans-1,2-cyclohexanediols, and cis- and trans-2-methoxycyclohexanols were determined in 0.25M sulfuric and 0.75M perchloric acids. The activation data for the cis- and trans-1,2-cyclohexanediols were consistent with reaction through a cyclic intermediate, since the entropy of activation for the trans-isomer was 6.4 cal. $deg.^{-1}$ $mole^{-1}$ less positive than for the cis. On the other hand, the energies and entropies of activation for cis- and trans-1,2-cyclopentanediols were practically identical, suggesting that the trans-isomer reacts via an acyclic mechanism.

The effect of total sulfate ion concentration was examined for the reactions of cis- and trans-1,2-cyclopentanediols in the range from 0.25M to 0.75M sulfuric acid. Perchloric acid was used to maintain constant acidity and ionic strength. The results indicate that $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$ participate in the reaction and that the rate constants increase as the number of sulfate ions in the cerium(IV)-sulfate complex decreases.

The carbonyl products of the oxidation reaction were characterized by formation of 2,4-dinitrophenylhydrazone derivatives directly from the reaction mixtures. Products were qualitatively identified by comparison of the infrared spectra and thin-layer chromatographic behaviors of these derivatives with the derivatives of known carbonyl compounds. The yields of products were determined from the weights of the derivatives. In general, reactions in which good pseudo-first-order kinetics were observed gave yields approaching 100%, whereas lower yields were obtained in the autocatalytic reactions. The cyclic 1,2-diols and 2-methoxy alcohols reacted with cerium(IV) by carbon-carbon bond cleavage to form dialdehydes whereas cyclohexanol and cyclopentanol formed the corresponding ketones.

The results of this study are related to the process of initiating graft polymerization onto cellulose by cerium(IV). The relative reactivities of trans-1,2-cyclohexanediol and of cyclohexanemethanol and tetrahydropyran-2-methanol were studied as models for the C_2-C_3 glycol group and C_6 hydroxyl, respectively. The glycol model reacted approximately 6 times faster than the models for the primary hydroxyl indicating that in the oxidation of cellulose with cerium(IV) the reaction will occur mainly, but not exclusively, at the C_2-C_3 glycol unit. The ring oxygen in tetrahydropyran-2-methanol had little effect on the rate of oxidation of the primary hydroxyl.

INTRODUCTION

In recent years there has been considerable interest in the possibility of modification of cellulosic materials by formation of graft copolymers. One interesting and promising method of initiating graft copolymerization onto cellulose and other polyhydroxy polymers is the ceric ion redox system first suggested by Mino and Kaizerman (1). The mechanism of initiation of graft polymerization by ceric ion is believed (1, 2) to involve formation of a complex between the ceric ion and the hydroxyls of the backbone polymer. This complex disproportionates forming a free radical on the backbone which then initiates polymerization of a vinyl monomer, M:

$$Ce(IV) + ROH \rightleftharpoons \text{Complex} \longrightarrow Ce(III) + H^+ + \dot{R}OH \text{ (or } RO\cdot)$$

$$\dot{R}OH + M \longrightarrow R(OH)M\cdot$$

$$R(OH)M\cdot + nM \longrightarrow R(OH)M\cdot_{n+1}$$

The polymerization reaction is terminated by oxidation of the free radical by cerium(IV).

The evidence for the proposed mechanism is derived primarily from studies of the reaction of ceric ion with simple organic compounds. The formation of cerium(IV)-alcohol complexes as intermediates in the oxidation reaction was first demonstrated quantitatively by Duke and co-workers (3, 4) in studies of the oxidation of 2,3-butanediol. The kinetics and mechanism of the polymerization reaction have been studied in ceric ion-alcohol systems using pinacol (5) and ethylene glycol (2) substrates. The formation of primary chemical bonds between the substrate and the vinyl graft polymer has been established with model (6, 7) and polymeric (8, 9) systems. Also, the incorporation of hydroxyl groups in polymers

formed in ethyl alcohol- and 2,3-butanediol-ceric ion systems indicates that the initiating species is the carbon radical, $\dot{R}OH$, rather than an alkoxy radical, RO· (6).

When cellulose is used as the backbone polymer it seems reasonable that the free radicals will be generated by reactions with the C_6 hydroxyl or C_2-C_3 glycol group, although the possibility of reactions at the cellulose end units should be considered. Terasaki and Matsuki (10) found a fast initial reaction in the ceric ion oxidation of cellulose and suggested that this rapid reaction corresponded to the C_1 linkage of the reducing end group. However, it has been shown that the high initial rate of reaction can be attributed to reaction of hydroxyls in the amorphous zones of cellulose (11). Also, in a recent study of several model compounds for cellulose it was concluded that since glucose is a more effective (as measured by rate of polymer formation) reducing agent than trans-1,2-cyclohexanediol, grafting may occur most easily at the hemiacetal end group (6). However, the greater effectiveness of glucose may be due to the greater number of glycol groups as well as the hemiacetal, and considering the relative occurrence of reducing end groups compared to the normal monomer unit it seems unlikely that significant reaction would occur at this location in cellulose.

Two studies of ceric-ion-initiated graft polymerization have suggested a special importance of 1,2-glycols in the reaction. In a study of the graft polymerization of acrylonitrile on methyl celluloses with varying degrees of substitution (0.66 to 1.87) it was found that grafting did not occur in the methyl celluloses containing no 1,2-glycols, whereas in the presence of such groups the reaction was quite rapid (11). Also, Mino, et al. (12) found that the ceric ion oxidation of polyvinyl alcohol occurred preferentially at the 1,2-glycol groups rather than at the normal 1,3-glycol units.

The special significance of the 1,2-glycol moiety in ceric ion initiated graft polymerizations may be related to the possibility of chelate formation. Although the formation of intermediate complexes in the reaction of ceric ion with 1,2-glycols has been demonstrated, the nature of these complexes is less well established. In his formulation of the theory of intermediate complex formation in oxidation Duke (13) assumed that when the reductant is 1,2-oxygenated it is necessarily bidentate and forms a chelate complex. The results of Offner (14, 15), in which the equilibrium constants for complex formation with cerium(IV) of diethylene glycol and several monohydric alcohols were compared, are in agreement with this assumption. On the other hand, Littler and Waters (16) concluded from studies of the relative rates of oxidation of certain glycols and their monomethyl ethers that cerium(IV) oxidations of 1,2-glycols proceed by an acyclic mechanism.

The purpose of this thesis was to evaluate the importance of chelate complex formation in the ceric oxidation of 1,2-glycols by examination of the kinetics and mechanism of oxidation of a series of cyclic alcohols and glycols. The possibility of chelate intermediates was assessed from studies of the reaction mechanisms of cis- and trans-1,2-cyclohexanediols and 1,2-cyclopentanediols, and certain monomethyl ethers of these compounds. For comparison the reactivities of single hydroxyls in cyclic systems were studied using cyclohexanol and cyclopentanol. In order to relate the results to the reactions occurring during the ceric ion-initiated graft polymerization onto cellulose, the reactivities of cyclohexanemethanol and tetrahydropyran-2-methanol were determined as models for the C_6 hydroxyl and compared to trans-1,2-cyclohexanediol which serves as a model for the C_2-C_3 glycol.

In the following sections some of the literature pertaining to oxidations of alcohols and glycols by cerium(IV) and related oxidants is reviewed. The nature

of cerium(IV) oxidation systems is considered, and the evidence concerning intermediate complexes in oxidation reactions is discussed.

THE NATURE OF CERIUM(IV) OXIDATION SYSTEMS

Quadrivalent cerium is a strong oxidizing agent, similar in strength to permanganate ion. The potential of the couple, Ce(III) = Ce(IV) + e, depends on the nature of the acid anion and the acid concentration as shown in Table I.

TABLE I

CERIUM(III)-CERIUM(IV) HALF-CELL POTENTIALS[a]

Acid Normality	Measured E			
	$HClO_4$	HNO_3	H_2SO_4	HCl
1	-1.70	-1.61	-1.44	-1.28
2	-1.71	-1.62	-1.44	--
4	-1.75	-1.61	-1.43	--
6	-1.82	-1.56	--	--
8	-1.87	--	-1.42	--

[a]Data from Reference (17).

These variations in potential reflect the formation of ionic complexes and have been used to determine the nature and stability of these complexes. At a given acid concentration, the oxidation potential decreases as the ability of the anion to form stable complexes increases. Thus, sulfate ion forms very stable complexes with cerium(IV) whereas perchlorate ion probably does not complex at all. The increase in the electrode potential with acid concentration in perchloric acid indicates hydrolysis equilibria. The opposite trend in nitric and sulfuric acids indicates that in these media further anion complexing of the cerium(IV) more than compensates for the effects of decreasing hydrolysis due to increased acidity.

Despite the fact that cerium(IV) solutions have been extensively studied, there is not complete agreement on the nature of the cerium(IV) species present in the various acid media. The evidence for complex formation is derived from determinations of the effect of concentration variables on the cerium(III)-cerium(IV) half-cell potential and on absorption spectra of cerium(IV) solutions. The nature of cerium(IV) in sulfuric and perchloric acid media has been examined most extensively, and the spectrophotometric studies of Hardwick and Robertson (18, 19) are generally considered to be most reliable.

Cerium(IV), in aqueous perchloric acid, exists as a number of hydrated ionic species, which may include Ce^{4+}, $CeOH^{3+}$, $Ce(OH)_2^{2+}$, and $(Ce\text{-}O\text{-}Ce)^{6+}$. The existence of hydrolyzed and dimeric species is well established (19-24), but there is less agreement on which hydrolyzed species are actually present in solution and on the magnitudes of the equilibrium constants involved. Sherrill, King, and Spooner (20) and Offner (14) favored the reaction

$$CeOH^{3+} + H_2O \rightleftarrows Ce(OH)_2^{2+} + H^+$$

for the hydrolysis equilibrium. On the other hand, Hardwick and Robertson interpreted their data assuming the hydrolysis reaction

$$Ce^{4+} + H_2O \rightleftarrows Ce(OH)^{3+} + H^+.$$

The dimerization of cerium(IV) probably occurs by the equilibrium

$$Ce(OH)^{3+} + Ce(OH)^{3+} \rightleftarrows (Ce\text{-}O\text{-}Ce)^{6+} + H_2O$$

and hence dimerization is favored by increases in the total cerium(IV) concentration and is usually negligible at low concentrations [ca. 10^{-3} M Ce(IV)].

Hardwick and Robertson (18) found that in 1.0N acid solutions (ionic strength = 2.0) ceric ion associated with sulfate ions to successively form $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$ according to the equilibria

$$Ce^{4+} + HSO_4^- \underset{}{\overset{K_1}{\rightleftharpoons}} Ce(SO_4)^{2+} + H^+$$

$$Ce(SO_4)^{2+} + HSO_4^- \overset{K_2}{\rightleftharpoons} Ce(SO_4)_2 + H^+$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} Ce(SO_4)_3^{2-} + H^+$$

and determined the complex formation constants, K_i, from spectrophotometric data at 25.0°C. Jones and Soper (25) had previously suggested the presence of $H_3Ce(OH)(SO_4)_3$, $H_2Ce(SO_4)_3$, and $H_4Ce(SO_4)_4$ complexes in sulfuric acid solutions of cerium(IV). However, Hardwick and Robertson showed that the ceric sulfate complexes do not contain hydrogen or hydroxyl ions since the absorbance of ceric ion solutions containing a fixed hydrogen ion to bisulfate ion ratio was unchanged over a range of acid concentrations.

The formation of complexes of cerium(IV) in acid solutions has a profound effect on the oxidation of organic compounds. In general, the oxidation rate decreases as the ability of the acid anion to form stable complexes with cerium(IV) increases. Thus, it was found in this work that the reaction of cis-1,2-cyclohexanediol was 3000 times faster in 1.0M perchloric acid than in mixed 0.25M sulfuric and 0.75M perchloric acids. Also, it has been shown that for many ceric ion oxidations the rate decreases with increases in sulfate ion concentration at constant acidity. The nature of the acid also affects the tendency of a given organic substrate to form kinetically and spectrophotometrically detectable complexes. Offner and Skoog (15) found consistently lower complex formation constants in nitric acid than in perchloric acid. Also, Muhammad and Rao (26, 27)

found that methanol is oxidized through an intermediate complex in perchloric acid, but were unable to find evidence for complex formation in sulfuric acid media.

MECHANISMS OF CERIUM(IV) AND RELATED OXIDATIONS

COMPLEX FORMATION IN OXIDATIONS OF OXYGENATED ORGANIC COMPOUNDS

The oxidation of oxygenated organic compounds by metal ions and metal ion complexes usually proceeds by direct transfer of electrons from the organic substrate to the metal ion. The electron transfer process often occurs as a disproportionation of a substrate-oxidant coordination complex, and Levitt (28) has suggested that such complexes are the common basis for all organic oxidations in acid solutions. Since the oxidant is, of necessity, an electron-seeking substance, usually a positive ion or a neutral molecule with a relatively positive charged atom, the initial site of oxidation will be a location of high electron density in the reductant. Thus, oxidations of oxygenated compounds probably proceed by mechanisms involving formation of stable complex intermediates or transition states in which a free electron pair of the oxygen is coordinately bonded to the oxidant.

A general theory of oxidation reactions was proposed by Duke (13) based on the hypothesis that coordination intermediates are necessary for the reaction. It is assumed that a coordination compound involving the oxidant, A, and reductant, B, is formed in a rapidly established equilibrium. The slow step in the reaction is the unimolecular decomposition of the coordination complex, C. If the complex formed involves one oxidant and one reductant molecule the reaction mechanism can be summarized:

$$A + B \overset{K}{\rightleftarrows} C \xrightarrow{k} \text{Products}$$

$$K = C/AB$$

where

$\underline{A}$ = concentration of the oxidant

$\underline{B}$ = concentration of the reductant

$\underline{C}$ = concentration of the coordination complex

$\underline{K}$ = complex formation constant

$\underline{k}$ = complex disproportionation rate constant

It can be shown that the rate of disappearance of total oxidant, $\underline{T}$, where $\underline{T} = \underline{A} + \underline{C}$, is given by the rate equation

$$-dT/dt = [kKB/(1 + KB)]T \qquad (1).$$

If the reductant is maintained in sufficient excess that the concentration of uncoordinated reductant, $\underline{B}$, is constant, the quantity in brackets in Equation (1) is constant and the rate expression becomes pseudo-first-order:

$$-dT/dt = k'T \qquad (2)$$

where

$$k' = kKB/(1 + KB) \qquad (3).$$

The equilibrium constant for complex formation and the rate constant for complex disproportionation can be experimentally evaluated by determining the pseudo-first-order rate constant, $\underline{k}'$, at a number of reductant concentrations. Then, since

$$1/k' = 1/k + 1/kKB \qquad (4)$$

$\underline{K}$ and $\underline{k}$ can be calculated from the slope and intercept of a plot of $1/\underline{k}'$ versus $1/\underline{B}$.

Observation of the kinetic form predicted by Duke's theory provides definite evidence for participation of intermediate complexes in the oxidation reaction

mechanism. However, the finding of ordinary second-order kinetics,

$$-dT/dt = k_{II}BT \qquad (5)$$

does not exclude the possibility of complex formation in the reaction. It can be seen from Equation (3) that if the complex equilibrium constant is small the term $\underline{KB}$ will be negligible compared to one, and the rate equation reduces to a second-order expression with

$$k_{II} = kK \qquad (6).$$

Second-order kinetics also results if complex formation is the rate-determining step and the complex therefore a reactive intermediate. In both of these situations the complex is considered to be an intermediate in the mechanism whose concentration is always very small. However, it is not possible to distinguish on the basis of kinetics alone between these mechanisms and alternate pathways not involving complexes as such which would give second-order kinetics. For example, a direct bimolecular oxidation mechanism, in which the oxidant-reductant interaction occurs as the reaction transition state, would also predict second-order kinetics.

The oxidation mechanism proposed by Duke has been observed in reactions with several oxidant types. Cerium(IV) oxidations of methanol (27), ethanol (29), 2,3-butanediol (3), glycerol (30), methyl ethyl ketone (31), and acetone (31) in perchloric acid, 2,3-butanediol (4) in nitric acid, and lactic acid (32) and cyclohexanol (33) in sulfuric acid all have been found to follow the kinetics predicted by Duke's intermediate complex theory. Kinetic and spectrophotometric evidence for complex formation has been obtained in oxidations of several 1,2-glycols by periodate ion (34-39). The oxidations of oxalate by trivalent

manganese (13) and pinacol (40) and certain organic acids (41-43) by manganic pyrophosphate have also been shown to proceed through complex intermediates.

On the other hand, many oxidation reactions observe second-order kinetics. Oxidations of 1,2-glycols by lead tetraacetate exhibit second-order kinetics, although intermediate complexes (cyclic and acyclic) are always postulated in these reactions (44, 45). While kinetic evidence of complex formation is obtained in many reactions with periodate ion, some compounds yield second-order kinetics. In the oxidation of 2-methyl-2,3-butanediol by periodate it was found that the cyclic intermediate is formed at a rate comparable with its breakdown to products (37), and it has been suggested that in periodate oxidations following second-order kinetics the formation of the intermediate is rate-determining (46).

The cerium(IV) oxidations of pinacol (5), methanol (26), glycerol (30), ethylene glycol (47), 2,3-butanediol (16), oxalate (48), and formaldehyde (49) all in sulfuric acid have been reported to be second-order. However, spectrophotometric evidence for complexes in the ceric sulfate oxidation of oxalate ion has recently been reported (50). The reaction of formaldehyde with cerium(IV) in perchloric acid (49) is also second-order. This reaction appears to be the only instance of a cerium(IV) oxidation in perchloric acid in which evidence for complexing was not obtained by Duke's method. In general, cerium(IV) oxidations exhibit a greater tendency for reaction through detectable complexes in perchloric and nitric acid media than in sulfuric acid. Muhammad and Rao (26, 27) have suggested that the mode of methanol oxidation is different in sulfuric acid than in perchloric acid. However, it is also possible that the frequent observation of second-order kinetics in oxidations in sulfuric acid media reflects a reduction in substrate-cerium(IV) complex stability constants due to formation of cerium(IV)-sulfate complexes.

In addition to the kinetic procedure developed by Duke, evidence for complex formation can also be obtained from spectrophotometric measurements, provided the spectrum of the complex differs significantly from that of the reactants. The color change in cerium(IV) solutions in perchloric and nitric acids which occurs on addition of alcohols and glycols is well known and is often used as a qualitative test for the alcohol functional group (51). Ardon (29), in a study of the reaction of ethanol and ceric perchlorate, developed a method for determination of the complex equilibrium constant from measurements of the change in the absorbance of cerium(IV) solutions at a number of alcohol concentrations. Values of the equilibrium constant for the ethanol-cerium(IV) complex determined from the spectrophotometric data agreed quite well with results from kinetic experiments. Ardon's method has been applied in the cerium(IV) oxidation of methanol (27), glycerol (30), methyl ethyl ketone and acetone (31) in perchloric acid and in all cases the agreement between the spectrophotometric and kinetic estimates of the equilibrium constant was excellent. Equilibrium constants for cerium(IV)-alcohol complexes were also determined from spectrophotometric measurements by Offner and Skoog (15), using a slightly different approach. The spectrophotometric methods are, of course, subject to the same limitations as the kinetic procedure in that small values of the equilibrium constant cannot be accurately determined.

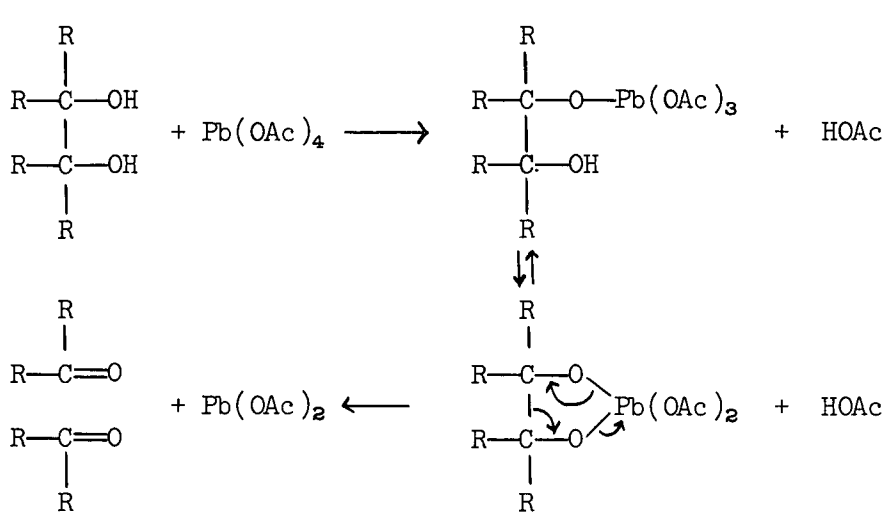
CHELATE COMPLEX FORMATION IN OXIDATION REACTIONS

There is considerable evidence (52, 53) that the formation of chelate rings, particularly five- and six-membered, enhances the stability of coordination complexes. The equilibrium constants for formation of complexes with bi- and tridentate ligands are larger than for complexes with the same type and number of donor atoms, but composed of monodentate ligands. The extra stability of chelates is believed to be due to a more positive entropy change in cyclic complex

formation (54). In forming a nonchelated complex each ligand displaces one water molecule from the coordination sphere of the central atom whereas each chelating ligand displaces two or more molecules. Thus, the total number of more or less independent species in the system and hence the disorder and entropy are increased when a chelate is formed.

In view of the extra stability of chelated complexes it seems reasonable to expect that whenever possible chelate complexes will be formed. Thus, it seems highly probable that in oxidations of 1,2-glycols, α-hydroxy acids and other 1,2-oxygenated compounds the intermediate complex will be a chelate structure with a 5-membered ring, except when steric requirements make formation of the chelate extremely difficult or impossible.

The possibility of chelate complex formation in oxidations of 1,2-oxygenated compounds has attracted considerable interest since cyclic intermediates were first proposed by Criegee (45, 55) in lead tetraacetate reactions. The cis-isomers of 1,2-cyclohexanediol and 1,2-cyclopentanediol were found to react faster than the corresponding trans-glycols (see Table II). Criegee and co-workers postulated the mechanism:



to account for these differences in reactivities. The relative reaction rates of these and several other cyclic cis- and trans-isomer pairs also have been correlated with the distance between the adjacent hydroxyl groups (56).

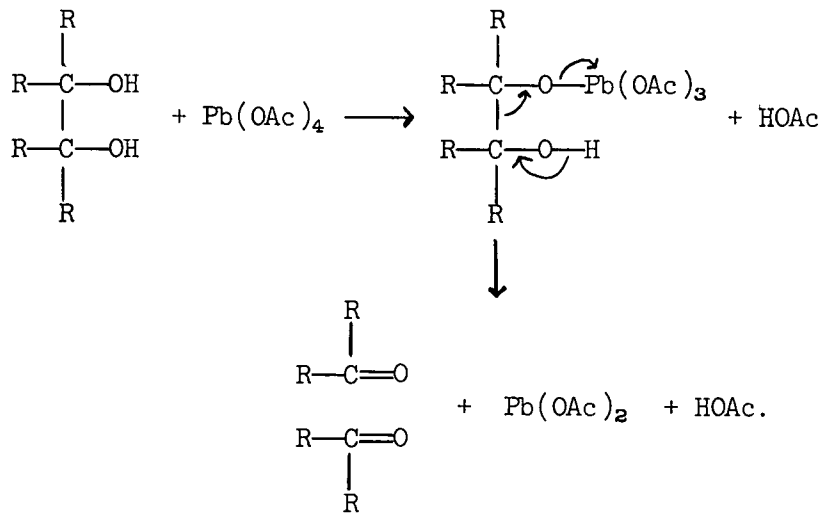
TABLE II

LEAD TETRAACETATE OXIDATIONS OF CYCLIC 1,2-GLYCOLS[a]

Substrate	Rate Constant[b]
cis-1,2-Cyclopentanediol	>40,000
trans-1,2-Cyclopentanediol	12.8
cis-1,2-Cyclohexanediol	5.0
trans-1,2-Cyclohexanediol	0.2

[a]Data from References (45) and (55).
[b]Second-order rate constants in acetic acid at 20°C.

There are, however, certain results which cannot be explained on the basis of the cyclic mechanism. Thus, trans-9,10-dihydrophenanthrene-9,10-diol, in which the hydroxyl groups are rigidly held in a diaxial orientation, and would therefore be able to form a cyclic intermediate only with considerable difficulty, is cleaved by lead tetraacetate more rapidly than the cis-isomer (57). Also, trans-9,10-decalindiol is oxidized by lead tetraacetate even though formation of a cyclic ester is impossible (55). These results, and the observed acid and base catalysis of lead tetraacetate reactions (44, 58, 59), can best be accounted for by an acyclic reaction mechanism:



The acyclic mechanism, however, does not explain the differences in the reactivities of cis- and trans-isomers. It seems likely therefore that lead tetraacetate oxidations of 1,2-glycols can proceed by both acyclic and cyclic pathways.

Like lead tetraacetate, periodic acid and sodium metaperiodate cleave 1,2-glycols to aldehydes and ketones, and cyclic intermediates have been proposed for this reaction. Price and Knell (60) found that cis-1,2-cyclohexanediol is oxidized by periodate faster than the trans-diol and suggested that the hydroxyls of the cis-isomer were more favorably oriented for complex formation. Later it was shown that the faster oxidation of the cis-isomer is due to a more rapid decomposition of the complex, not to a greater ease of complex formation (39). The equilibrium constant for cyclic complex formation was actually larger for the trans than for the cis (1000 versus 410 at pH 8.8) and this result was shown to be consistent with considerations of the iodine-oxygen bond lengths in the octahedral periodate anion, $H_3IO_6^{2-}$, and the steric requirements of the cyclic complex. Unlike lead tetraacetate, periodate does not react with compounds such as trans-9,10-decalindiol in which cyclic complex formation is impossible (61, 62). Further evidence for cyclic intermediates in periodate oxidation has been obtained from studies of methyl-substituted ethylene glycols (34) and 1,2-cyclopentanediols (46).

Rocek and Westheimer (63) found that chromic acid oxidizes cis-1,2-dimethyl-1,2-cyclopentanediol 1700 times faster than the trans-diol and proposed a cyclic chromic acid ester to account for these differences in reaction velocity. A chelate complex was suggested by Littler, et al. (64) for the oxidation of pinacol by vanadium(V) since pinacol is oxidized 16 times faster than pinacol monomethyl ether. On the other hand, cerium(IV) oxidizes pinacol and pinacol monomethyl ether at about the same rate and these authors concluded that a chelate complex was not involved (16). Furthermore, only slight differences were found in the rates of oxidation of ethanol, 2-methoxyethanol, and ethylene glycol.

The results obtained by Littler and Waters (16) for cerium(IV) oxidations of the ethanol, 2-methoxyethanol, and ethylene glycol are shown in Fig. 1. While the over-all rates for these compounds are quite similar, the rate constants for the monohydric alcohols decrease with increasing substrate concentration whereas the opposite behavior is observed for the 1,2-glycol. This fact may be more significant than the over-all similarity of the rates, and may reflect chelate complex formation with the ethylene glycol. However, it would seem that more data, particularly in a lower concentration range, where complex formation constants could be determined, should be obtained before definite conclusions are made concerning the nature of the complexes in these reactions.

The possibility of chelate complex formation with cerium(IV) is clearly indicated in the results of Offner (14, 15). Thus, as shown in Table III, the equilibrium constants for diethylene glycol and 1,3-butanediol, which can form 5- and 6-membered chelate rings, respectively, are significantly higher than for the monohydric alcohols and for 1,4-butanediol which would require a 7-membered ring to form a chelate.

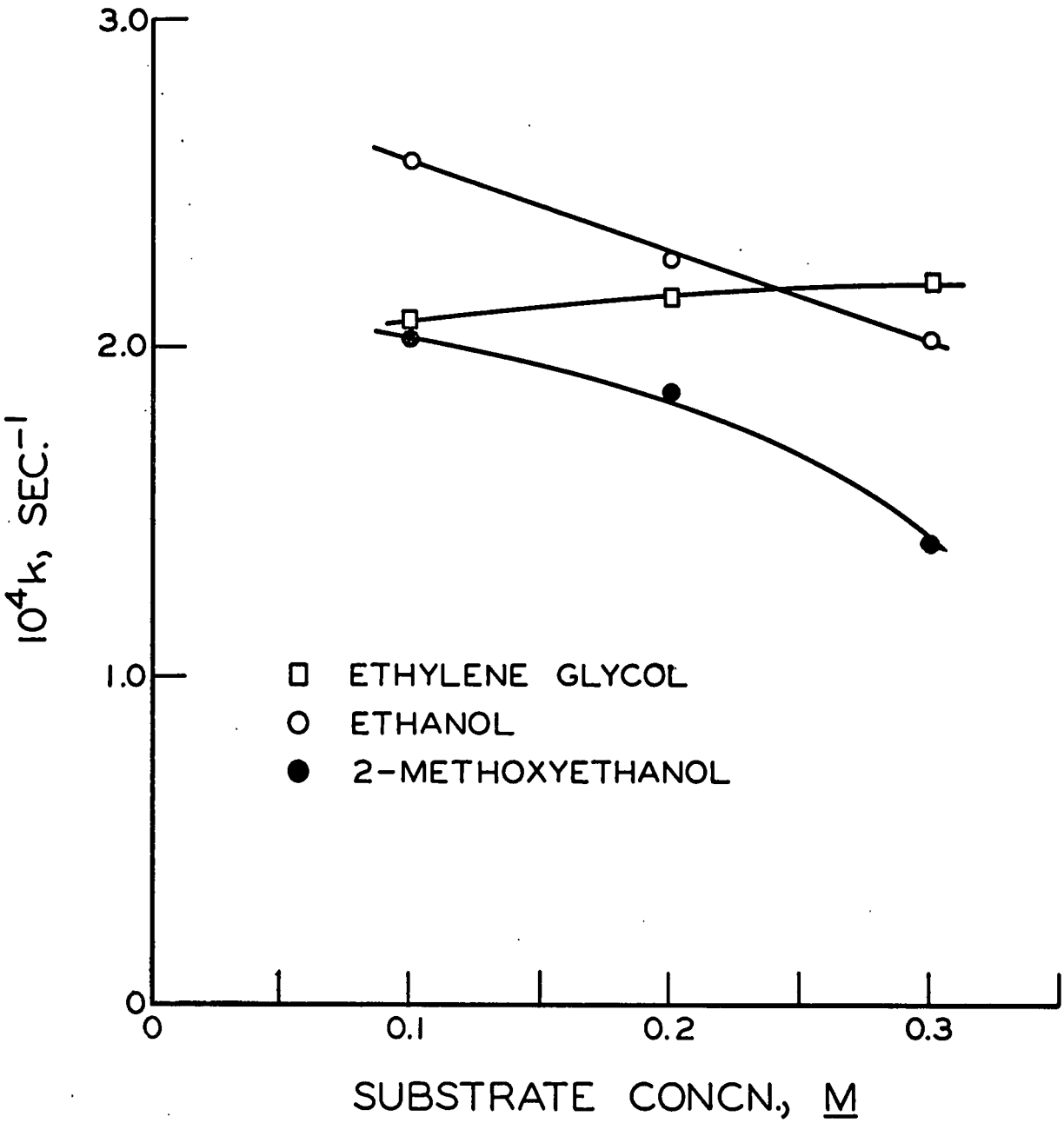


Figure 1. Cerium(IV) Oxidations in 0.272M Sulfuric Acid (16)

TABLE III

EQUILIBRIUM CONSTANTS FOR COMPLEX FORMATION WITH CERIUM(IV)

Substrate	Equilibrium Constant	
	1.69M $HClO_4$	2.0M HNO_3
tert-Butanol	13.2	0.61
sec-Butanol	11.4	0.99
n-Butanol	15.8	0.99
Diethyleneglycol	40.0	3.2
1,3-Butanediol	29.7	3.1
1,4-Butanediol	14.3	2.6

Thus, there is considerable evidence which suggests the importance of cyclic intermediates in reactions of 1,2-glycols. However, the nature of the intermediate in cerium(IV) oxidations is uncertain. The results of Littler and Waters indicated that cerium(IV) oxidizes 1,2-glycols through acyclic complexes. On the other hand, Offner's results suggest the possibility of chelate complex formation with cerium(IV). The nature of the intermediates formed in oxidations of 1,2-glycols by cerium(IV) was evaluated in this work from studies of the mechanism of oxidation of cyclic alcohols, glycols, and monomethyl ethers of the glycols.

EXPERIMENTAL PROCEDURES

PREPARATION AND PURIFICATION OF COMPOUNDS

Whenever available, compounds were purchased from chemical supply companies and purified by recrystallization or fractional distillation. Most other compounds were prepared by known reactions. In some cases preparations were carried out by analogy to literature preparations of similar compounds. Detailed procedures for these reactions are given in Appendix I. A Nester/Faust 18-inch spinning band distillation column was used for all fractional distillations. Melting points were determined using total immersion thermometers calibrated by the National Bureau of Standards. Infrared spectra were obtained for all organic compounds used in this thesis and the spectra examined for consistency with the proposed structure. In general, however, literature spectra were not available for direct comparison.

SOURCE OF ORGANIC REACTANTS

cis-1,2-Cyclohexanediol

cis-1,2-Cyclohexanediol was prepared by the permanganate oxidation of cyclohexene (Matheson, Coleman and Bell) according to the method of Clarke and Owen (65). The diol was purified by recrystallization from benzene, m.p. 99.4-100°C. [lit. m.p. 98°C. (65)].

trans-1,2-Cyclohexanediol

trans-1,2-Cyclohexanediol was purchased from Aldrich Chemical Company and purified by several recrystallizations from benzene, m.p. 103.5-104.1°C. [lit. m.p. 101.5-103.0°C. (66)].

Cyclohexanemethanol

Cyclohexanemethanol, purchased from Aldrich Chemical Co., was purified by fractional distillation, b.p. 86.5°C. at 17.5 mm.

Cyclohexanol

A sample of cyclohexanol, purified by Schroeder (67), was further purified by fractional distillation, b.p. 159.5°C.

cis-1,2-Cyclopentanediol

cis-1,2-Cyclopentanediol was prepared from cyclopentene (Special Products Division, Phillips Petroleum Company; Research grade) by permanganate oxidation according to the procedure of Owen and Smith (68). The diol was purified by fractional distillation, b.p. 119.5°C. at 19 mm. [lit. b.p. 88-92°C. at 2 mm. (68) and 105-6°C. at 10 mm. (69)]; m.p. 31.8-32.5°C. [lit. m.p. 29.8-30.5°C. (69)].

trans-1,2-Cyclopentanediol

trans-1,2-Cyclopentanediol was prepared by the peroxyformic acid oxidation of cyclopentene by the method of Owen and Smith (68) and was purified by fractional distillation, b.p. 81.5-82.0°C. at 0.43 mm. [lit. b.p. 93°C. at 2 mm. (68) and 101°C. at 1.5 mm. (69)]; m.p. 54.2-54.6°C. [lit. m.p. 50°C. (68) and 53.7°C. (69)].

Cyclopentanol

Cyclopentanol (Aldrich Chemical Co.) was purified by fractional distillation at atmospheric pressure, b.p. 139°C.

cis-2-Methoxycyclohexanol

cis-2-Methoxycyclohexanol was prepared from the trans-isomer by the procedure of Buck, et al. (70). The literature procedure was modified by eliminating distillation of the intermediate mesylate and benzoate derivatives. The product was

purified by preparative gas chromatography using a Wilkens Instrument Aerograph "Autoprep" gas chromatograph. A 10 ft. by 3/8 inch 20% Hyprose on chromosorb W column was used at 125°C. and 100 ml. He/min. flow rate. The retention time of the cis-isomer was 34 min. whereas the trans-isomer gave a retention time of 41.6 min.

trans-2-Methoxycyclohexanol

trans-2-Methoxycyclohexanol was prepared from cyclohexene oxide (Aldrich Chemical Co.) by the acid-catalyzed addition of methanol (71). The product was fractionally distilled, b.p. 88°C. at 23 mm. [lit. b.p. 72.5-73.2°C. at 10 mm. (71) and 91.5-93.0°C. at 24 mm. (72)]. When attempts were made to prepare aqueous solutions of the distilled product, cloudy solutions resulted. The alcohol was therefore purified further by preparative gas chromatography using a 10 ft. by 3/8 inch 20% Hyprose on chromosorb W column at 145°C. and 100 ml. He/min. flow rate (retention time 18 min.). The gas chromatography-purified alcohol was readily soluble in water.

trans-2-Methoxycyclopentanol

Cyclopentene oxide was prepared by the peroxybenzoic acid oxidation of cyclopentene (73). The cyclopentene oxide was converted to trans-2-methoxycyclopentanol by the acid-catalyzed addition of methanol using a procedure analogous to the preparation of trans-2-methoxycyclohexanol. The trans-2-methoxycyclopentanol was purified by fractional distillation, b.p. 93°C. at 22 mm. [lit. b.p. 96°C. at 27 mm. (74)]. The details of this preparation are given in Appendix I.

Tetrahydropyran-2-methanol

Tetrahydropyran-2-methanol (Aldrich Chemical Co.) was purified by fractional distillation, b.p. 81°C. at 18 mm.

SOURCE OF REACTION PRODUCTS

Adipaldehyde

Adipaldehyde was prepared for use as a known in the product analysis experiments by the sodium bismuthate oxidation of trans-1,2-cyclohexanediol (75). The product was fractionally distilled, b.p. 82°C. at 7 mm. [lit. b.p. 97.5°C. at 12 mm. (75)].

1,2-Cyclohexanedione

1,2-Cyclohexanedione was purchased from Aldrich Chemical Co. and used, without purification, in the preparation of the bis(2,4-dinitrophenylhydrazone) derivative.

Cyclohexanone

Cyclohexanone purchased from Aldrich Chemical Co. was fractionally distilled before use, b.p. 53°C. at 20 mm.

Cyclopentanone

Cyclopentanone (Aldrich Chemical Co.) was purified by fractional distillation, b.p. 35°C. at 20.5 mm.

Glutaraldehyde

Glutaraldehyde was purchased from Aldrich Chemical Co. in the form of a 25% aqueous solution. This solution was used directly in the preparation of glutaraldehyde bis(cis-1,2-cyclopentanediol acetal) (see Appendix I). A pure sample of glutaraldehyde was prepared for use in quantitative product analysis by fractional distillation of the 25% solution, b.p. 76-77°C. at 1.5 mm. Standard solutions were prepared by dissolving a weighed amount of the freshly distilled glutaraldehyde in water. The pure liquid dialdehyde very rapidly becomes a viscous, water-insoluble polymer on standing.

2-Methoxycyclohexanone

2-Methoxycyclohexanone was prepared for use as a reference in product analysis experiments by the oxidation of trans-2-methoxycyclohexanol with dichromate in acetic acid. The procedure used was adapted from a similar preparation of cyclohexanone from cyclohexanol given by Fieser (76). The preparation of 2-methoxycyclohexanone by dichromate oxidation has been reported previously (77). Further details on this preparation are given in Appendix I.

PREPARATION OF SOLUTIONS FOR KINETICS AND PRODUCT ANALYSIS

REACTION MEDIA

Perchloric and sulfuric acids, and mixtures of these acids, were used as the reaction media in all the cerium(IV) oxidation reactions. Stock solutions of these acids (2.0M) were prepared from reagent-grade concentrated sulfuric acid and 70% perchloric acid and standardized with a standard sodium hydroxide solution. Reaction media were prepared by volumetric dilution of these stock solutions. Ordinary distilled water was redistilled from alkaline permanganate and dilute sulfuric acid for use in the preparation of all solutions.

CERIUM(IV) SOLUTIONS

A stock solution, 0.1M in cerium(IV), was prepared by dissolving ceric sulfate [$Ce(HSO_4)_4$; G. Frederick Smith Chemical Co.] in 0.5M sulfuric acid. This stock solution was used in the preparation of the cerium(IV) solutions for all reactions in sulfate-containing media.

A second stock solution, 0.05M cerium(IV) in 1.0M perchloric acid, was prepared by appropriate dilution of a ceric perchlorate solution [ca. 0.5M cerium(IV) in 6M perchloric acid] purchased from G. Frederick Smith Chemical Co. The exact

cerium(IV) and acid concentrations of the commercial reagent were determined by procedures given by Offner (14). The cerium(IV) solutions used in all reactions in 1.0M perchloric acid were prepared from this stock solution.

The titers of cerium(IV) solutions were determined by titration of weighed samples of primary standard arsenic trioxide using osmium tetroxide as a catalyst and 1,10-phenanthroline as the indicator (78).

SOLUTIONS OF ORGANIC SUBSTRATES

The organic substrate solutions used in the product analysis and kinetic experiments were prepared by dissolving weighed samples of the pure compounds in appropriate amounts of water and acid. Two stock solutions were prepared of each compound. These solutions were then diluted volumetrically to the concentration desired for the particular experiment.

Many of the compounds used in this work were hygroscopic. To minimize absorption of water during weighing, the distillation fractions of these substances were collected and stored in 4-ml. vials and weighed out by rapidly transferring the contents of the vial to a tared stoppered flask.

PRODUCT ANALYSIS PROCEDURES

ATTEMPTS TO ISOLATE AND IDENTIFY REACTION PRODUCTS BY ETHER EXTRACTION AND GAS CHROMATOGRAPHY

In the first attempts to isolate the reaction products of the cerium(IV) oxidations, reaction mixtures were extracted continuously with ether (usually 48 hr.), the ether extracts dried and concentrated, and the residues examined by gas chromatography. There were two important difficulties with this procedure. First, to prevent secondary oxidations of the reaction products it was desirable to use

a high substrate to cerium(IV) concentration ratio. It was necessary, therefore, to use rather large quantities of the organic reactant to prepare detectable amounts of the reaction product. Second, there was always the possibility of changing the nature of the reaction product during the isolation procedure. The products of ceric ion oxidations of alcohols are carbonyl compounds and some of them, especially the dialdehydes adipaldehyde and glutaraldehyde, are not particularly stable. This method of product analysis was abandoned in favor of the direct determination of carbonyl products as 2,4-dinitrophenylhydrazone derivatives.

DETERMINATION OF CARBONYL PRODUCTS AS 2,4-DINITROPHENYLHYDRAZONES

Qualitative identifications and quantitative determinations of the carbonyl products of cerium(IV) oxidation reactions were made by formation of 2,4-dinitrophenylhydrazone derivatives. These derivatives can be formed directly in the reaction mixtures thus avoiding the problems associated with isolation of products. Also, only very small quantities (ca. 2.5×10^{-4} mole) of the product were necessary for the determination.

The quantitative determination is based on the fact that the reactions of 2,4-dinitrophenylhydrazine with carbonyl functional groups are rapid, nearly quantitative and result in high molecular weight derivatives which are insoluble in aqueous solutions. Qualitative identification of the carbonyl product was made by comparison of the infrared spectra and chromatographic behavior of the product 2,4-dinitrophenylhydrazones with derivatives of known compounds.

The experimental procedure used in the 2,4-dinitrophenylhydrazone determinations was based on the work of Iddles and Jackson (79). In a typical determination, 10 ml. of 0.05M cerium(IV) solution were added to 40 ml. of 0.125M substrate solution and the reaction allowed to proceed to completion. The reaction mixture was

then added slowly with stirring to 50 ml. of a saturated solution of 2,4-dinitrophenylhydrazine in 2N hydrochloric acid. After storing 1 hr. in an ice bath the precipitate was collected in a tared fine porosity fritted glass crucible, washed with 2N hydrochloric acid and water, and dried in a vacuum desiccator over Drierite. From the weight of the precipitate the yield was calculated.

Infrared spectra were obtained of the 2,4-dinitrophenylhydrazones of the reaction products and of several known aldehydes and ketones considered to be possible reaction products. The spectra were run by the Institute's analytical department using the potassium bromide pellet technique.

The precipitates were also examined by thin-layer chromatography using Eastman Chromatogram Sheets Type K301R. The plates were developed in either 95:5 benzene-ethyl acetate or 95:5 benzene-petroleum ether (b.p. 60-110°C.). Qualitative product identifications were made by comparison of the movement of the 2,4-dinitrophenylhydrazone with that of knowns run on the same sheet. The solvent systems used were sufficiently sensitive to permit essentially unambiguous identifications of the products.

PROCEDURES FOR KINETIC MEASUREMENTS

GENERAL CONSIDERATIONS IN THE DESIGN OF THE KINETIC EXPERIMENTS

All kinetic experiments were carried out with the organic reductant in excess over the cerium(IV) so that the reactions would be pseudo-first-order. This technique offers two important advantages in the study of this type of oxidation reaction. First, this procedure reduces the possibility of complications due to the further oxidation of the primary reaction products. Second, if the reaction proceeds through an intermediate complex, the equilibrium constant for formation of

the complex may be conveniently determined by varying the excess of the organic substrate (provided the equilibrium constant is sufficiently large).

Nearly all kinetic experiments were run in duplicate. The results of the individual experiments are tabulated in Appendix III. The precision of the kinetic experiments depended to a large measure on the type of kinetics observed. For reactions obeying good pseudo-first-order kinetics the average deviation in the rate constants for duplicate runs was usually quite small (less than 3%). On the other hand, the rate constants for the autocatalytic reactions were, in general, less reproducible.

EXPERIMENTAL PROCEDURES

Titrimetric Rate Determinations

A solution (45 ml.) of the organic substrate in the desired acid medium was thermostated in a water bath maintained at 14.9 ± 0.1°C. After 30 minutes, 5 ml. of 0.1M cerium(IV) in the same acid and at the temperature of the bath were added. The reaction mixture was stirred and a stopwatch was started. At recorded time intervals, 5-ml. aliquots of the reaction solution were withdrawn and quenched in 5 ml. of 0.01M ferrous sulfate solution in 50 ml. of 0.5M sulfuric acid. The excess ferrous ion was titrated with 0.01M cerium(IV) in 0.5M sulfuric acid using 1,10-phenanthroline as an indicator. The concentration of cerium(IV) in the reaction mixture was determined from the titers of the ferrous sulfate quench and the ceric sulfate titrant, and the rate constants were calculated from the concentration versus time data.

Spectrophotometric Rate Determinations

Reaction rates were determined by following the absorbance of the reaction mixture using a Cary Model 15 recording spectrophotometer. The reaction mixtures

were prepared as follows. Five milliliters of a cerium(IV) solution of the appropriate concentration in the desired acid medium were placed in an ampoule made by blowing thin one end of a 20-cm. length of 11-mm. glass tubing. The ampoule was placed in 20 ml. of a solution of the desired concentrations of organic substrate and acid contained in a 19 by 3 cm. test tube. The test tube was placed in a constant temperature bath and after 30 minutes the reaction was initiated by breaking the thin-walled bulb and mixing the reactants. A sample of the reaction mixture was immediately transferred to the spectrophotometer cell and the recording of the absorbance-time curve was begun. For reactions in which absolute zero time measurements were required for estimation of the initial absorbance, the time lag between mixing the reactants and the beginning of the absorbance recording was measured with a stopwatch.

The reaction temperature in the spectrophotometer cell was maintained constant by circulating water from a bath through a Cary thermostatable cell jacket (No. 1540750). Water from the constant temperature bath was also circulated through the cell compartment walls. The temperatures reported are the mean of the temperatures measured at the inlet and outlet of the cell jacket. Temperature fluctuations at the inlet and outlet were less than $\pm$ 0.03°C., and the reaction temperatures are conservatively estimated to be accurate to $\pm$ 0.1°C.

The absorbance of the reaction solution was followed at a fixed wavelength. The wavelength used depended on the initial cerium(IV) concentration and was chosen to give a reasonably large initial absorbance. The wavelengths most frequently used were 317.5 and 400 mμ for initial cerium(IV) concentrations of 0.00025M and 0.001M, respectively, in mixed sulfuric and perchloric acids, and 425 mμ for 0.0025M cerium(IV) in 1.0M perchloric acid.

The spectrophotometric method of rate determination is based on the fact that the absorbance of cerium(IV) solutions is directly proportional to the cerium(IV) concentration. The adherence to Beer's Law was demonstrated for the solutions used in this work and the spectrophotometer was shown to be linear over the range from 0 to 2 absorbance. Data for cerium(IV) solutions in 0.5M sulfuric acid at 400 mμ and 15.0°C. is given in Fig. 2 and in Table XXXI (Appendix III). Since all reactions were run under conditions of pseudo-first-order kinetics, molar absorptivities were not necessary for calculation of the rate constants and were therefore not determined for all the conditions used. Cerium(III) and the organic compounds used have negligible absorbances at the concentrations and wavelengths used.

Comparison of Titrimetric and Spectrophotometric Methods

The primary purpose of the titrimetric rate determinations was to demonstrate the applicability of the indirect spectrophotometric method by comparison to a method involving direct measurement of the ceric ion concentration. Pseudo-first-order rate constants were determined by the two methods for the reaction of cis-1,2-cyclopentanediol in 0.5M sulfuric acid at 14.8 to 14.9°C. Second-order rate constants determined from the values of the pseudo-first-order rate constant at several diol concentrations were 0.926 and 0.938 liter $mole^{-1}$ $min.^{-1}$ for the spectrophotometric and titrimetric methods, respectively. Thus, the two methods give comparable results and the more convenient spectrophotometric method was used in all other rate determinations. Similar agreement between these two methods was reported by Ardon (29).

TREATMENT OF THE KINETIC DATA

Pseudo-First-Order Rate Constants

For oxidation reactions carried out with all reactants except cerium(IV) present in large excess the kinetics become pseudo-first-order and the rate

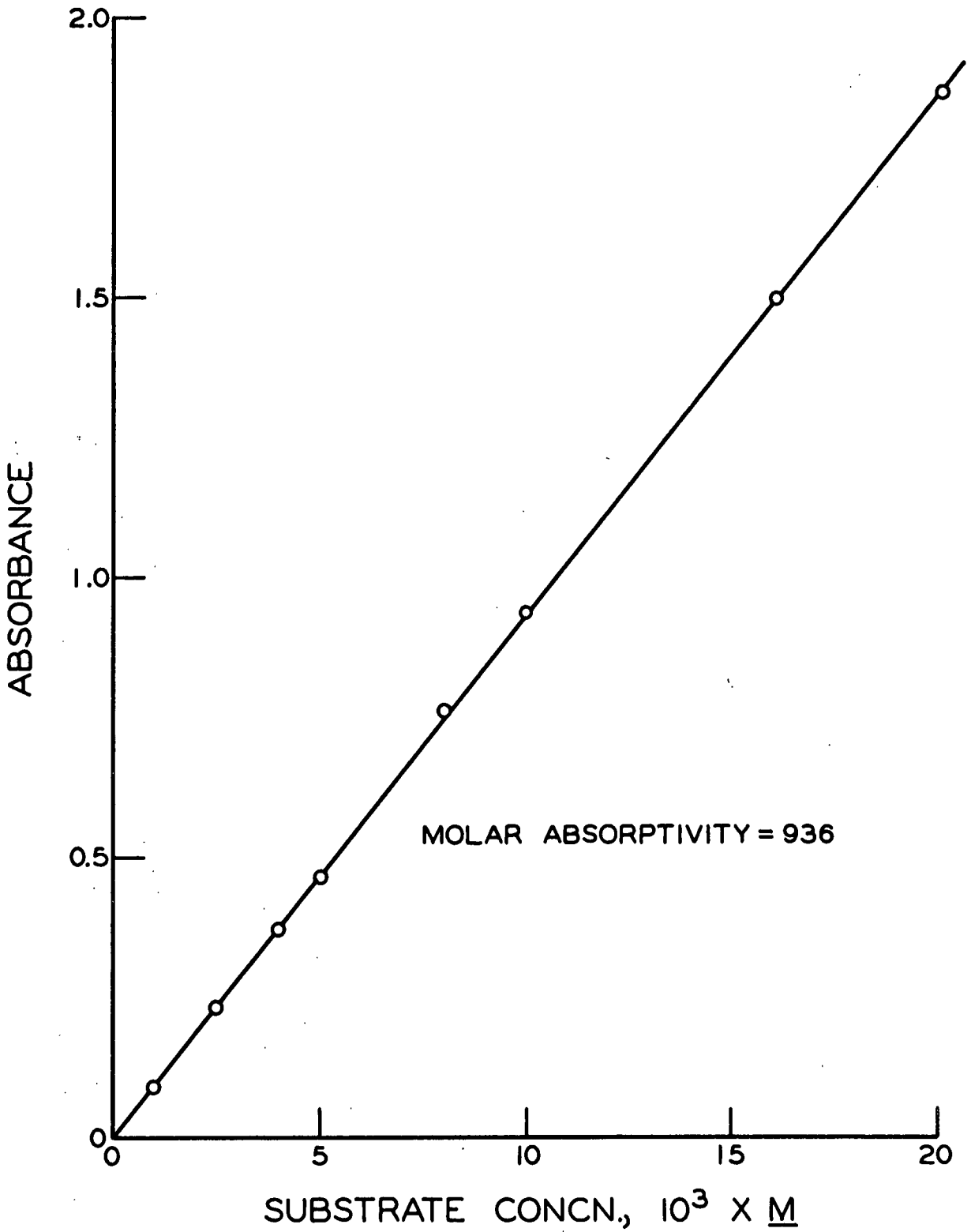


Figure 2. Determination of Molar Absorptivity of Cerium(IV) in 0.5M Sulfuric Acid at 400 mμ and 15.0°C.

expression is

$$-dCe(IV)/dt = k'Ce(IV) \qquad (7),$$

where

Ce(IV) = total cerium(IV) concentration

k' = pseudo-first-order rate constant

Integration of the rate expression gives

$$Ce(IV) = Ce(IV)_o \exp(-k't) \qquad (8)$$

or

$$\ln [Ce(IV)/Ce(IV)_o] = -k't \qquad (9)$$

where

$Ce(IV)_o$ = initial total cerium(IV) concentration.

The pseudo-first-order rate constant can be determined from a plot of $\ln [Ce(IV)/Ce(IV)_o]$ versus time. However, for convenience a computer program was devised to calculate k' using a least squares regression technique. The exponential form of the integrated rate expression was used in the regression analysis since use of the logarithmic form gives unequal statistical weights to the data (larger weights are given to the lower concentrations) (80).

Since the integrated rate expression for a first-order reaction involves a ratio of concentrations, any linear function of the cerium(IV) concentration may be used in place of the concentration. Thus, in the spectrophotometric kinetic experiments the absorbance of the reaction solution was used directly in the calculation of k'.

Initial Pseudo-First-Order Rate Constants

For certain reactions carried out under pseudo-first-order conditions the plots of the logarithm of the absorbance versus time showed considerable deviation

from linearity. In most cases, after an initial linear portion, the slope of the plot increased at an increasing rate. For these reactions initial pseudo-first-order rate constants, k_i', were calculated.

Several attempts were made to develop an analytic technique for calculation of the initial rate constants. In general, it was found that the analytic methods did not always give reasonable estimates of the initial linear portion of the ln A versus time plots. The analytic methods and results obtained are discussed in more detail in Appendix II. Because of the failure of analytic methods the initial rates were calculated simply from the slope of a line drawn through the initial linear portion of a plot of ln A versus time.

The precision of rate constants for reactions requiring the initial rate calculation was considerably less than for reactions obeying good pseudo-first-order kinetics. This lower precision is probably the result of the complexity of the reaction as well as the subjectivity of the method of calculating the initial rates.

Second-Order Rate Constants

For reactions which are first order with respect to two reactants, the pseudo-first-order rate constant is

$$k' = k_{II}S \qquad (10)$$

where

k_{II} = second-order rate constant

S = concentration of reactant in excess.

Second-order rate constants were calculated by two methods. When experiments were carried out at several levels of substrate concentration, the second-order rate constant was determined from the slope of a least squares linear regression

of k' versus S. For reactions run at only one substrate concentration, an estimate of the second-order rate constant was obtained by dividing the pseudo-first-order rate constant by the substrate concentration. Rate constants calculated by the latter procedure are referred to as "apparent" second-order rate constants or simply k'/substrate concentration, since the order of reaction with respect to substrate concentration was not rigorously established in these cases.

Evaluation of Complex Formation Constants

Equilibrium constants for the formation of ceric ion-substrate complexes were determined by kinetic and spectrophotometric techniques. The methods of calculation of the equilibrium constant from the two types of data are quite similar. The equilibrium constants were calculated from the slope and intercept, determined by a least squares linear regression, of a "reciprocal" plot. [See Discussion and Results section (p. 48 and 68) for a discussion of the equations involved.]

In evaluating the equilibrium constant from these reciprocal plots it is necessary to use the concentration of uncoordinated substrate in the reaction mixture. This concentration differs from the initial substrate concentration by the amount of the substrate involved in the complex and was calculated by a method of successive approximations. The initial substrate concentrations were used to obtain a first estimate of the equilibrium constant. The substrate concentrations were then corrected using the first estimate of the equilibrium constant and the following equations, derived for a 1:1 substrate-cerium(IV) complex:

$$S = S_o - C \qquad (11)$$

and

$$C = KSCe(IV)_o/(1 + KS) \qquad (12)$$

where

$\underline{S}$ = equilibrium substrate concentration

$\underline{S}_o$ = initial substrate concentration

$\underline{C}$ = complex concentration

$\underline{K}$ = equilibrium constant

$\underline{Ce(IV)}_o$ = initial total cerium(IV) concentration.

A second estimate of the equilibrium constant was then obtained using the corrected substrate concentration and the process was repeated until successive repetitions produced no change in the equilibrium constant.

Thermodynamic Functions of Activation

The integrated form of the Arrhenius equation is

$$k = Z \exp(-E_a/RT) \qquad (13)$$

where

$\underline{k}$ = rate constant

$\underline{Z}$ = Arrhenius frequency factor

$\underline{E_a}$ = energy of activation, cal. mole^{-1}

$\underline{R}$ = gas constant, 1.987 cal. mole^{-1} deg.$^{-1}$

$\underline{T}$ = absolute temperature

or, in logarithm form

$$\ln k = \ln Z - E_a/RT \qquad (14)$$

and thus for reactions exhibiting Arrhenius temperature dependence, a plot of ln $\underline{k}$ versus $1/\underline{T}$ is linear with slope $-\underline{E_a}/\underline{R}$ and intercept ln $\underline{Z}$. The energies of activation and the frequency factors were obtained from values of the slopes and intercepts of the Arrhenius plots calculated by the method of least squares.

Second-order rate constants with units of liter mole^{-1} sec.$^{-1}$ were used in these calculations.

Transition state theory gives the following equation relating the rate constant and the entropy and enthalpy of activation (81).

$$k = (k_B T/h) \exp(-\Delta H^{\ddagger}/RT) \exp(\Delta S^{\ddagger}/R) \qquad (15)$$

where

k_B = Boltzmann constant, 1.3803×10^{-16} erg deg.$^{-1}$

h = Planck's constant, 6.625×10^{-27} erg sec.

$\Delta H^{\ddagger}$ = enthalpy of activation, cal. mole^{-1}

$\Delta S^{\ddagger}$ = entropy of activation, cal. mole^{-1} deg.$^{-1}$

For reactions in solutions (81)

$$\Delta H^{\ddagger} = E_a - RT \qquad (16)$$

and thus

$$k = (ek_B T/h) \exp(-E_a/RT) \exp(\Delta S^{\ddagger}/R) \qquad (17).$$

Taking logarithms and inserting numerical values for k_B, h, and e, the base of Naperian logarithms, yields

$$\ln k = \ln T - E_a/RT + \Delta S^{\ddagger}/R + 24.76 \qquad (18).$$

Substituting the Arrhenius expression for ln k and rearranging gives

$$\Delta S^{\ddagger}/R = \ln Z - \ln T - 24.76 \qquad (19)$$

or

$$\Delta S^{\ddagger} = R \ln(Z/T) - 49.2 \qquad (20).$$

The entropies of activation were calculated from this equation and the values of the frequency factor, Z, obtained from the Arrhenius correlations.

RESULTS AND DISCUSSION

PRODUCT ANALYSIS AND REACTION STOICHIOMETRY

The oxidation of alcohols to aldehydes and ketones involves the removal of two electrons and two hydrogen ions. Since cerium(IV) is a one-electron oxidant, two moles of cerium(IV) are reduced for every mole of alcohol oxidized. Cerium(IV) oxidations of alcohols take place in two stages. The first stage, which may include formation of a complex in a prior equilibrium, is rate-determining and involves the abstraction of one electron and release of one hydrogen ion from the alcohol to form a free radical intermediate. This free radical is then very rapidly oxidized by a second cerium(IV) to the carbonyl product. In the oxidation of 1,2-glycols the first step also involves cleavage of the carbon-carbon bond. The nature of the pathway of cerium(IV) oxidations of several simple alcohols and glycols is illustrated in Table IV.

The formation of free radicals as intermediates in cerium(IV) oxidations of organic compounds is well established. Quantitative evidence for free radical formation is given by Mino, Kaizerman, and Rasmussen (5), who showed that in the ceric sulfate-pinacol reaction the ratio of cerium(IV) consumed to acetone formed changed from 1.0 to 2.0 when acrylamide was added to the reaction system. In contrast to lead tetraacetate and periodate, which are specific oxidants for glycols, cerium(IV) is capable of oxidizing, in addition to glycols and alcohols, a variety of organic compounds, including aldehydes and ketones. Furthermore, the rates of oxidation of aldehydes and ketones are often comparable to those of alcohols and glycols. Thus, secondary reactions of the initial product can be quite important in cerium(IV) oxidations of alcohols and glycols.

TABLE IV

REACTION STOICHIOMETRY AND PRODUCTS FOR SOME CERIUM(IV) OXIDATIONS OF SIMPLE ALCOHOLS AND GLYCOLS

1. Methanol (26, 27).

$$CH_3OH + Ce(IV) \longrightarrow CH_3O\cdot + Ce(III) + H^+$$

$$CH_3O\cdot + Ce(IV) \longrightarrow H_2C{=}O + Ce(III) + H^+$$

2. 2,3-Butanediol (3, 4).

$$CH_3\overset{OH}{\overset{|}{C}}H-\overset{OH}{\overset{|}{C}}HCH_3 + Ce(IV) \longrightarrow CH_3C\overset{O}{\underset{H}{<}} + \cdot\overset{OH}{\overset{|}{C}}HCH_3 + Ce(III) + H^+$$

$$CH_3\dot{C}HOH + Ce(IV) \longrightarrow CH_3C\overset{O}{\underset{H}{<}} + Ce(III) + H^+$$

3. Pinacol (5).

$$(CH_3)_2\overset{HO}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}(CH_3)_2 + Ce(IV) \longrightarrow (CH_3)_2C{=}O + \cdot\overset{OH}{\overset{|}{C}}(CH_3)_2 + Ce(III) + H^+$$

$$(CH_3)_2\overset{OH}{\overset{|}{C}}\cdot + Ce(IV) \longrightarrow (CH_3)_2C{=}O + Ce(III) + H^+$$

DETERMINATION OF CARBONYL PRODUCTS AS 2,4-DINITROPHENYLHYDRAZONES

Since the products of cerium(IV) oxidations of alcohols and glycols are carbonyl compounds, the products could be qualitatively identified and quantitatively determined by conversion to 2,4-dinitrophenylhydrazone derivatives. It is possible that products containing functional groups other than carbonyl could arise in cerium(IV) oxidations, particularly from secondary reactions of the primary products. However, since this work was concerned with the initial two-electron oxidation of alcohols and glycols, attention was focused on the carbonyl reaction products.

Determination of Known Carbonyl Compounds

The reaction of 2,4-dinitrophenylhydrazine with carbonyl compounds occurs according to the equation

$$RR'C{=}O + H_2NNHC_6H_3(NO_2)_2 \longrightarrow RR'C{=}NNHC_6H_3(NO_2)_2 + H_2O.$$

The 2,4-dinitrophenylhydrazone derivatives are essentially insoluble in aqueous media, and thus the reaction can be used for quantitative gravimetric analysis. Literature data for a wide variety of carbonyl compounds indicate that yields of 95 to 100% are normally obtained (82).

The method of formation of the 2,4-dinitrophenylhydrazone derivatives used in this work was a modification of a procedure given by Iddles and Jackson (79). The accuracy of the method was tested by determination of several known compounds under conditions similar to the reaction systems. The per cent recoveries of the known compounds are summarized in Table V. The results of these experiments show that reasonably quantitative determinations of products can be obtained by this method.

TABLE V

DETERMINATION OF KNOWN COMPOUNDS AS 2,4-DINITROPHENYLHYDRAZONES[a]

Substrate	Conditions	Recovery, %
Adipaldehyde	0.00552M in 1.0M perchloric acid	96.0
Cyclohexanone	0.00515M in 1.0M perchloric acid	92.4 91.5
Cyclopentanone	0.00489M in 0.25M sulfuric and 0.75M perchloric acids	93.0 92.6
Glutaraldehyde	0.00625M in water	102.3 101.2
Glutaraldehyde	0.0075M in 0.1M aqueous trans-1,2-cyclopentanediol	100.6

[a]Further details of these experiments are given in Table XVI in Appendix III.

Determination of Carbonyl Reaction Products

The 2,4-dinitrophenylhydrazone derivatives of the carbonyl reaction products were formed directly from the reaction mixtures. The products were identified by comparison of the infrared spectra and thin-layer chromatographic behaviors of these derivatives with those of known compounds. The yield of product was calculated from the weight of the 2,4-dinitrophenylhydrazone formed. The results of the product analysis experiments are summarized in Table VI.

Since the qualitative identification of products was based on comparisons with known compounds, it was necessary to consider what compounds could be formed in cerium(IV) oxidations. The product of cyclohexanol oxidation has been shown to be cyclohexanone in sulfate-containing media (83) and for this compound it was necessary only to show that the same product is formed in 1.0M perchloric acid. By analogy to cyclohexanol, cyclopentanol would be expected to produce cyclopentanone. Since 1,2-ethanediol, 2,3-butanediol, and pinacol all yield the corresponding cleavage products [formaldehyde (47), acetaldehyde (4), and acetone (5), respectively], the most likely products from the 1,2-cyclohexanediols and 1,2-cyclopentanediols would be the corresponding dialdehydes, adipaldehyde, and glutaraldehyde. However, the 2-hydroxy ketones, adipoin, and 2-hydroxycyclopentanone would result if the diols reacted by secondary alcohol oxidation. The ceric ion oxidation of the 2-methoxy alcohols, pinacol monomethyl ether, and 2-methoxyethanol has been studied (16) but the products of these reactions were not reported. As with the 1,2-diols, it seems likely that the 2-methoxycycloalkanols would react either by secondary alcohol oxidation to form 2-methoxycycloalkanones or by cleavage reactions to form dialdehydes and methanol.

For comparison standards the 2,4-dinitrophenylhydrazones of adipaldehyde, glutaraldehyde, cyclohexanone, cyclopentanone, 1,2-cyclohexanedione, and

TABLE VI

DETERMINATION OF CARBONYL PRODUCTS OF CERIUM(IV) OXIDATIONS AS 2,4-DINITROPHENYLHYDRAZONES[a]

Substrate	Yield, % Reactants N_2 Purged	Yield, % No N_2 Purge	Products
1. Reactions in 1.0M Perchloric Acid			
Cyclohexanol	69.3 72.3	71	Cyclohexanone
Cyclopentanol	--	89.5	Cyclopentanone
cis-1,2-Cyclohexanediol	98.5 98.5	86.4	Adipaldehyde
trans-1,2-Cyclohexanediol	89.8 91.4	81.9	Adipaldehyde
trans-2-Methoxycyclohexanol	54.8[b] 55.1[b]	50[b]	Adipaldehyde and formaldehyde
2. Reactions in 0.25M Sulfuric and 0.75M Perchloric Acids			
Cyclopentanol	57.1 54.8	-- --	Cyclopentanone
trans-1,2-Cyclohexanediol [diol/Ce(IV) = 700][d]	67.4[b]	--	Adipaldehyde and unknown[c]
trans-1,2-Cyclohexanediol [diol/Ce(IV) = 10][d]	24.3[b] 27.7[b]	-- --	Adipaldehyde and unknown[c]
trans-1,2-Cyclopentanediol	103.3 103.1	98.5	Glutaraldehyde
cis-2-Methoxycyclohexanol	24.9[b]	--	Adipaldehyde and unknown[c]
trans-2-Methoxycyclohexanol	17.4[b]	--	Adipaldehyde
trans-2-Methoxycyclopentanol	104.5 105.2	98.5	Glutaraldehyde
3. Reactions in 0.5M Sulfuric Acid			
trans-1,2-Cyclopentanediol	--	101.6 100.8	Glutaraldehyde

[a] Further details of these experiments are given in Table XVII in Appendix III.
[b] Yields for reactions producing more than one product are based on the primary product and thus are only very approximate.
[c] The unknown formed in reactions producing adipaldehyde was shown to be a product of the cerium(IV) oxidation of adipaldehyde.
[d] The substrate to cerium(IV) concentration ratio normally was ten.

2-methoxycyclohexanone were prepared. The 1,2-cyclohexanedione derivative was prepared since adipoin is known to be oxidized by 2,4-dinitrophenylhydrazine to form 1,2-cyclohexanedione bis(2,4-dinitrophenylhydrazone) (84). 2-Methoxycyclohexanone undergoes a similar reaction with 2,4-dinitrophenylhydrazine, but, depending on the conditions, can also form 2-methoxycyclohexanone 2,4-dinitrophenylhydrazone (85, 86). The derivative of this compound was therefore prepared under conditions similar to those encountered in the reaction mixtures.

The infrared spectra of the known 2,4-dinitrophenylhydrazone derivatives are, as would be expected, quite similar. There were, however, characteristic differences in the numbers and positions of the absorption bands, particularly in the fingerprint region. Thus, it was possible to make reasonably positive identifications of the derivatives of the reaction products by comparison to the known spectra. The reactions of cis- and trans-1,2-cyclohexanediols in 1.0M perchloric acid, and of these diols and cis- and trans-2-methoxycyclohexanols in 0.25M sulfuric and 0.75M perchloric acids gave adipaldehyde as the product. The reactions of cyclohexanol and cyclopentanol produced the corresponding ketones, cyclohexanone and cyclopentanone. Glutaraldehyde was formed in the oxidation of trans-1,2-cyclopentanediol and trans-2-methoxycyclopentanol. The 2,4-dinitrophenylhydrazone from the reaction of trans-2-methoxycyclohexanol in 1.0M perchloric acid, however, gave a spectrum which could not be matched with any of the available knowns. Also, in certain cases the spectra of the product 2,4-dinitrophenylhydrazones were not as well defined as the known compounds suggesting some impurities in the former. This problem was particularly noticeable in reactions producing adipaldehyde in the sulfate-containing media.

One problem which often accompanies the preparation of 2,4-dinitrophenylhydrazones is coprecipitation of the reagent. 2,4-Dinitrophenylhydrazine has

two absorption bands (at 980 and 707 $cm.^{-1}$) which are not present in any of the 2,4-dinitrophenylhydrazone derivatives, and thus, it appears that little or none of the reagent was coprecipitated in the preparation of these derivatives.

The results of thin-layer chromatography confirmed the conclusions drawn from the infrared spectra. However, the precipitates from oxidations of trans-1,2-cyclohexanediol, and cis- and trans-2-methoxycyclohexanol in 0.25M sulfuric and 0.75M perchloric acid were found to contain a second product in addition to the adipaldehyde derivative. This additional product was shown to be the product of oxidation of adipaldehyde by cerium(IV). The presence of this product in these reactions is quite reasonable since the kinetics for these reactions were autocatalytic.

The precipitate of the products from the reaction of trans-2-methoxycyclohexanol in 1.0M perchloric acid was shown by thin-layer chromatography to contain adipaldehyde and a second product. This second product was not the adipaldehyde oxidation product mentioned above and was later shown to be formaldehyde. When the infrared spectrum of the precipitate from this reaction was re-examined, it was found that all bands could be accounted for either by adipaldehyde or formaldehyde 2,4-dinitrophenylhydrazones. Also, all bands required by these compounds were found in the product spectrum. The formaldehyde is apparently the result of oxidation of the methanol formed from the cleavage of 2-methoxycyclohexanol to adipaldehyde.

In order to calculate the yields of the reactions it is necessary to know the stoichiometry and the reaction product. In all cases it was assumed that two moles of cerium(IV) produce one mole of carbonyl product. For reactions producing a single product the moles of product formed are given by the weight of precipitate divided by the molecular weight of the product 2,4-dinitrophenylhydrazone, and the

yield is given by

$$\% \text{ yield} = \frac{\text{moles product}}{1/2 \text{ moles cerium(IV) consumed}} \times 100 \qquad (21).$$

For reactions producing more than one product a rigorous calculation of the yield would require a knowledge of the proportions of each product and the stoichiometry of the reactions producing each product. However, a very approximate estimate of the yield can be obtained by basing the calculation on the major product.

The yields determined in the product analysis experiments correlated quite well with the behavior in the kinetic experiments. Thus, those reactions giving good pseudo-first-order kinetics gave yields approaching 100%, whereas low yields were obtained in the autocatalytic reactions. For the reactions of trans-1,2-cyclohexanediol in 0.25M sulfuric and 0.75M perchloric acid it was shown that a 70-fold increase in the diol to cerium(IV) concentration ratio increases the yield from 25 to 67%.

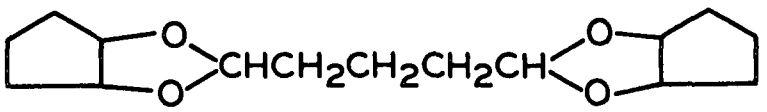
In Table II the effect of oxygen on the yield of product is also shown for several reactions. The presence of oxygen in the reaction mixtures in most instances reduced the yield. This fact suggests that oxygen affects cerium(IV) reactions by changing the nature of the products formed. Possibly the oxygen is captured by the free radicals produced as intermediates in the cerium(IV) oxidation, forming peroxy free radicals (87) which react to form different products.

OXIDATION PRODUCT FOR THE cis-1,2-CYCLOPENTANEDIOL REACTION

By analogy to the reaction of the trans-isomer, cis-1,2-cyclopentanediol would be expected to form glutaraldehyde as the reaction product. However, in an attempt to prepare the 2,4-dinitrophenylhydrazone from a cis-1,2-cyclopentanediol reaction mixture a very low weight of precipitate was obtained. Later it was

found that on storage of cis-1,2-cyclopentanediol-cerium(IV) reaction mixtures overnight at 0°C. a white crystalline precipitate is formed. Similar treatment of a synthetic mixture of cis-1,2-cyclopentanediol and known glutaraldehyde also produced crystals. The crystalline products from the reaction mixtures and the known cis-1,2-cyclopentanediol-glutaraldehyde solution were isolated and shown to be identical by comparison of infrared spectra, melting points, and mixed melting points. It was concluded, therefore, that the primary product of the reaction of cis-1,2-cyclopentanediol with cerium(IV) is glutaraldehyde, but that this product reacts with the diol to form a secondary product.

The infrared spectrum of the crystalline material showed no carbonyl absorption band, and only a weak hydroxyl band, which could be due to absorbed water. It seems likely, therefore, that the secondary product was glutaraldehyde bis(cis-1,2-cyclopentanediol acetal):



A larger quantity of this material was prepared from cis-1,2-cyclopentanediol and known glutaraldehyde for characterization by molecular weight and carbon and hydrogen determinations (see Appendix I). The results of these analyses were consistent with the structure proposed above: mol. wt. 271; C, 67.39%, H, 8.92% (calcd. for $C_{15}H_{24}O_4$, mol. wt. 268.4; C, 67.14%, H, 9.01%).

KINETICS AND MECHANISM OF CERIUM(IV) OXIDATIONS

CERIUM(IV) OXIDATION MECHANISMS

Since ceric ion oxidations involve the transfer of an electron from the organic reductant to cerium(IV), it seems reasonable that the reaction mechanism

will include an interaction between cerium(IV) and the reductant. Two types of mechanisms can be distinguished depending on the nature of this interaction. In the first mechanism, a coordination complex is formed between the organic substrate and cerium(IV) in a prior equilibrium step. The intermediate complex then disproportionates unimolecularly in the rate-determining step forming cerous ion and a free radical:

$$Ce(IV) + S \underset{}{\overset{K}{\rightleftharpoons}} C \xrightarrow{k} R\cdot + Ce(III) + H^+$$

$$Ce(IV) + R\cdot \xrightarrow{fast} Product + Ce(III) + H^+$$

The free radical is rapidly oxidized by a second cerium(IV). It is assumed that the coordination equilibrium is rapidly established and that equilibrium is maintained despite the unidirectional disproportionation of the complex. In the second mechanism the substrate is oxidized directly by cerium(IV). In this case the interaction occurs in the transition state:

$$Ce(IV) + S \longrightarrow \underset{\text{transition state}}{[Ce(IV)\text{---}S]} \longrightarrow R\cdot + Ce(III) + H^+ .$$

As in the first mechanism the free radical formed is rapidly oxidized.

The intermediate complex mechanism was first proposed for and applied to cerium(IV) oxidations by Duke and co-workers (3, 4, 13). The mechanism predicts the rate expression*

$$-dCe(IV)/dt = [kKS/(1 + KS)]\, Ce(IV) \qquad (22)$$

*A rigorous analysis of the complex formation mechanism, in which the steady-state approximation is applied to the concentration of the free radical, gives

$$-dCe(IV)/dt = 2kKSCe(IV)/(1 + KS)$$

However, the factor of two is usually incorporated into the rate constant.

where Ce(IV) represents the total cerium(IV) concentration [i.e., free cerium(IV) plus cerium(IV) in complex]. As discussed in the introduction, the oxidations of many compounds by cerium(IV) conform to this kinetic expression. On the other hand, the direct oxidation mechanism implies second-order kinetics*:

$$- dCe(IV)/dt = k_{II}SCe(IV) \qquad (23)$$

where k_{II} is the second-order rate constant.

Both of the mechanisms for cerium(IV) oxidations discussed above predict kinetic expressions first-order with respect to the cerium(IV) concentration, and, experimentally, cerium(IV) oxidations always give first-order kinetics. On the other hand, the dependence of the rate on the substrate concentration indicated by the two types of mechanisms is quite different. The difference in the dependence on substrate concentration provides the means for distinguishing between the mechanisms. In both cases, when the substrate is present in large excess the reaction becomes pseudo-first-order. The pseudo-first-order rate constant then is a function of the substrate concentration, the nature of the functional relationship depending on the particular mechanism of oxidation. It can be seen from Equation (22) that the theory of intermediate complex formation predicts

$$k' = kKS/(1 + KS) \qquad (24)$$

and

$$1/k' = 1/k + 1/kKS \qquad (25).$$

The direct oxidation theory (and in certain cases the complex formation theory) implies a linear dependence of the pseudo-first-order rate constant on substrate concentration, i.e., $k' = k_{II}S$.

*As with the complex formation mechanism, a factor of two has been incorporated into the rate constant.

There are several important variations of the complex formation theory to be considered. In addition to the 1:1 substrate-cerium(IV) complex indicated above there is also the possibility of complexes involving two or more substrate molecules. For example, in the reaction of 2,3-butanediol, evidence for the formation of polyglycolated species was obtained (3, 4). These higher complexes are apparently less reactive than the monoglycolated species. Further, there are two cases in which reactions proceeding through intermediate complexes would give ordinary second-order kinetics. First, if the equilibrium constant is small, then the term KS in the denominator of Equation (24) will be small compared to one, and the rate expression reduces to second-order kinetics. Second, if complex formation is not rapid but rather is rate-determining, second-order kinetics will result and the rate constant will refer to the rate of complex formation.

It is apparent from the above discussion that two types of rate expressions may be observed in cerium(IV) oxidation reactions. When a reaction proceeds according to Equation (22), positive evidence for complex formation is obtained. On the other hand, second-order kinetics [Equation (23)] can result from several reaction mechanisms. In this case, it is not possible to distinguish between the alternate pathways by kinetic methods.

ORDER OF REACTION WITH RESPECT TO CERIUM(IV) CONCENTRATION

Pseudo-First-Order Reactions

In the presence of a large excess of the organic substrate the rate of disappearance of cerium(IV) should be first-order:

$$- dCe(IV)/dt = k'Ce(IV) \qquad (25)$$

and hence

$$\ln [Ce(IV)/Ce(IV)_o] = - k't \qquad (26)$$

and, since the absorbance, A, is a linear function of the cerium(IV) concentration:

$$\ln (A/A_o) = - k't \qquad (27).$$

Thus, a plot of ln (A/A_o) versus time should be linear with slope -k'.

The reactions of cis- and trans-1,2-cyclopentanediols in a number of acid media, all containing sulfate ions, always gave excellent pseudo-first-order kinetics. Similarly, the reactions of trans-2-methoxycyclopentanol in 0.25M sulfuric and 0.75M perchloric acids were found to be pseudo-first-order. In 1.0M perchloric acid, the reactions of cis- and trans-1,2-cyclohexanediols and trans-2-methoxycyclohexanol also obeyed pseudo-first-order kinetics, giving reasonably linear plots of ln (A/A_o) versus time. Some typical logarithm plots for the pseudo-first-order reactions are given in Fig. 3 and 4.

The fact that the logarithm plots for these reactions are linear shows that the order of reaction with respect to cerium(IV) is one. As a further test of the first-order dependence it was shown for the reactions of cis- and trans-1,2-cyclopentanediols in 0.25M sulfuric and 0.75M perchloric acids that the pseudo-first-order rate constant is independent of the initial cerium(IV) concentration. The results of these experiments are given in Table VII. The rate constants are essentially independent of the initial cerium(IV) concentration, although there is a slight decrease in k' as $Ce(IV)_o$ increases. This decrease in the rate constant probably reflects the failure of the assumption of constant substrate concentration at the higher cerium(IV) concentrations.

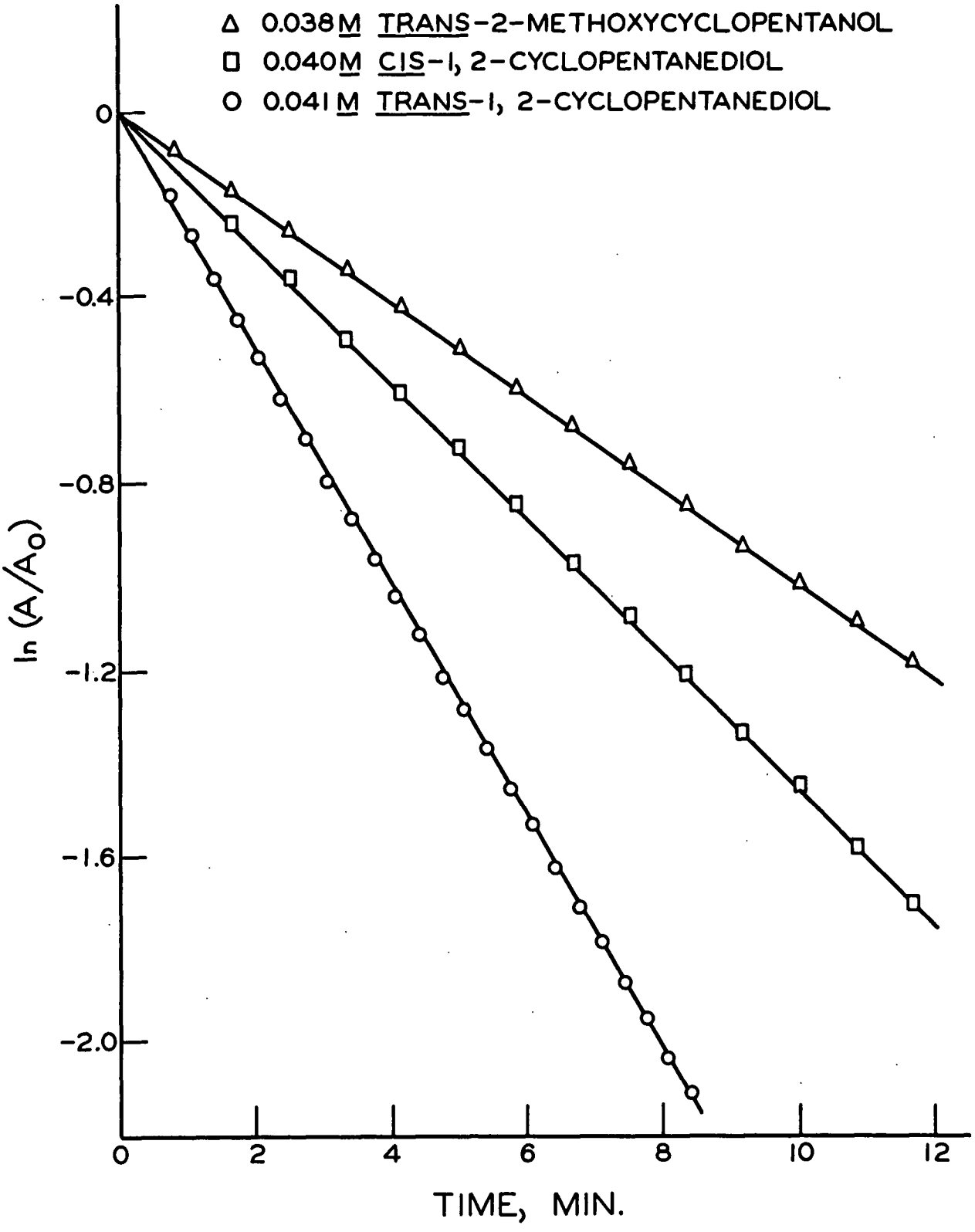


Figure 3. Typical Pseudo-First-Order Reactions in 0.25M Sulfuric and 0.75M Perchloric Acids at 15.0°C. Initial Cerium(IV) Concentration, 0.00025M

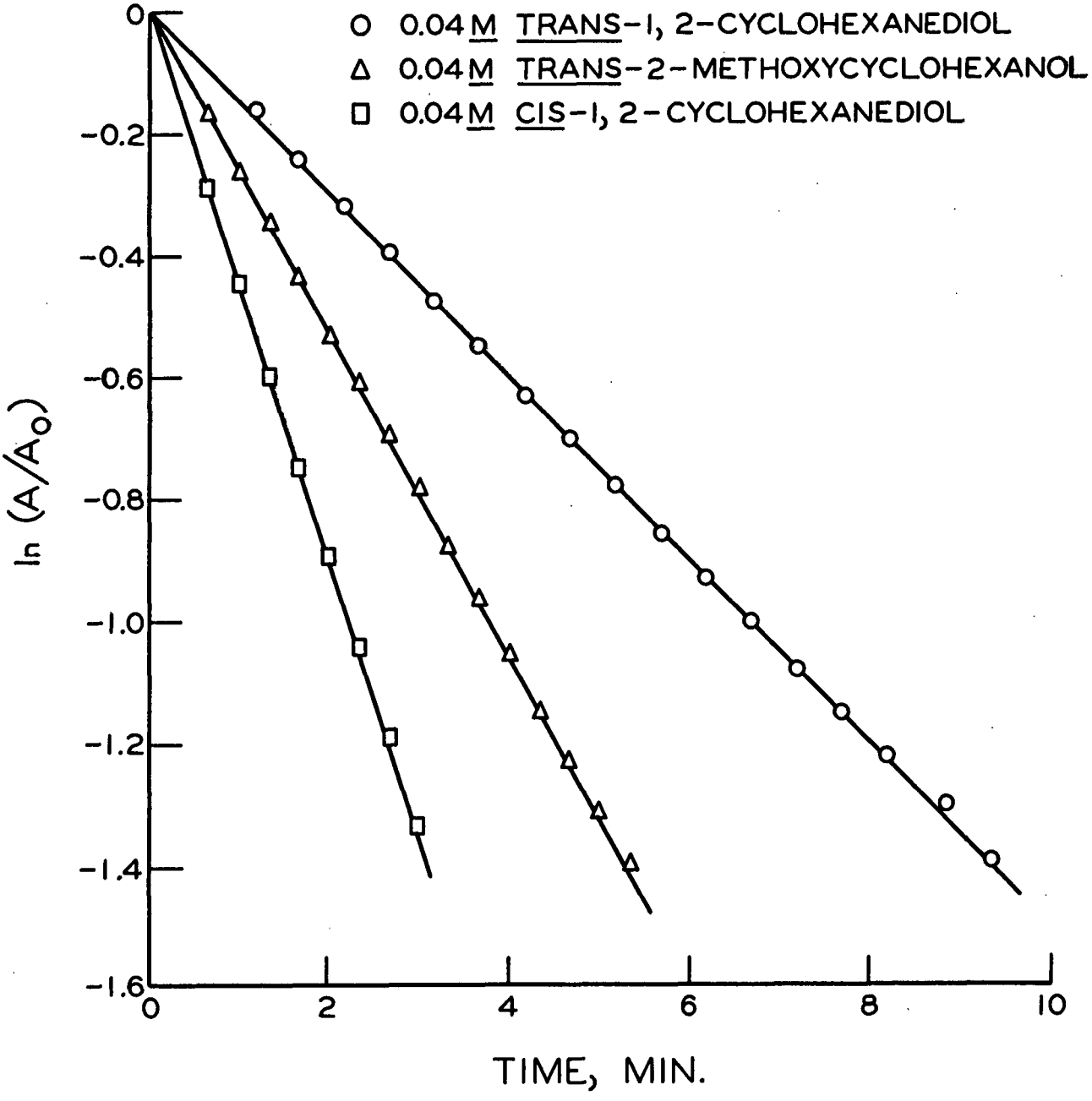


Figure 4. Typical Pseudo-First-Order Reaction in 1.0M Perchloric Acid at 15.0°C. Initial Cerium(IV) Concentration, 0.0025M

TABLE VII

EFFECT OF THE INITIAL CERIUM(IV) CONCENTRATION ON THE PSEUDO-FIRST-ORDER RATE CONSTANT FOR REACTIONS OF *cis*- AND *trans*-1,2-CYCLOPENTANEDIOLS[a]

Initial Cerium(IV) Concn., M	k', min.$^{-1}$	
	cis	*trans*
0.005	0.0529	--
0.001	0.0576	0.0966
0.0005	0.0578	0.0992
0.00025	0.0590	0.0990

[a]Reactions 0.016M in substrate in 0.025M sulfuric and 0.75M perchloric acids at 15.0°C. Rate constants are the average of two experiments. Data for individual runs are given in Tables XXXIII and XXXIV in Appendix III.

Autocatalytic Reactions

Despite the fact that all reactions were run with an excess of the organic substrate and thus should have given pseudo-first-order kinetics, the plots of ln (A/A_o) versus time for many reactions were found to deviate significantly from linearity. In these reactions the slope of logarithm plot increased with time, suggesting that oxidation of the initial reaction product was contributing to the over-all rate of disappearance of cerium(IV).

The reactions of *cis*- and *trans*-1,2-cyclohexanediol, *cis*- and *trans*-2-methoxycyclohexanol, cyclohexanol and cyclopentanol in 0.25M sulfuric and 0.75M perchloric acids all exhibited autocatalysis of the type described above. In these reactions at least a 40-fold excess of substrate was used. Several autocatalytic reactions are illustrated in Fig. 5.

The reactions of cyclohexanol in 1.0M perchloric acid exhibited a slightly different type of deviation from pseudo-first-order kinetics. Examples of these reactions are shown in Fig. 6. At the higher cyclohexanol concentrations the

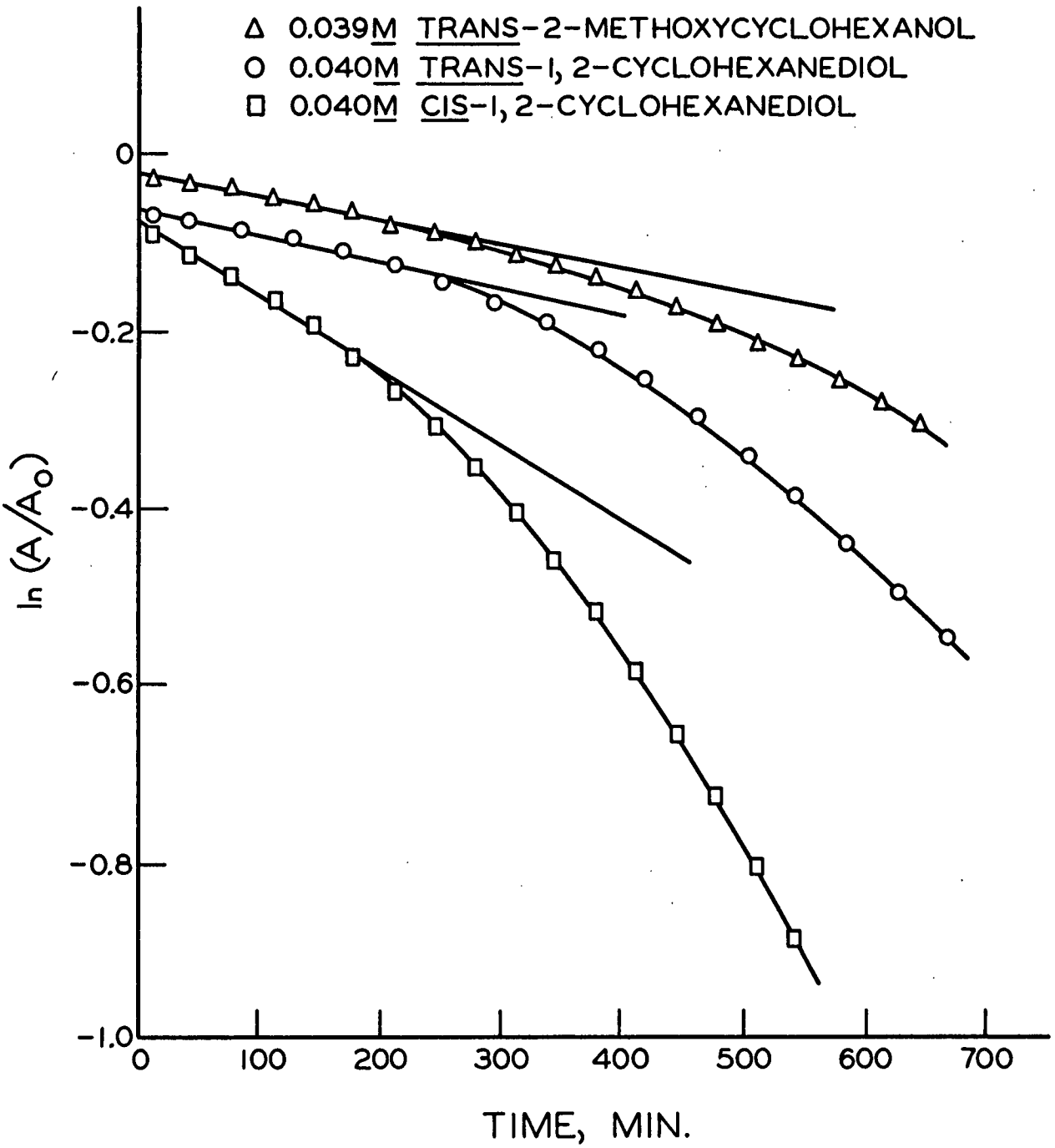


Figure 5. Typical Autocatalytic Reactions in 0.25M Sulfuric and 0.75M Perchloric Acids at 20.0°C. Initial Cerium(IV) Concentration, 0.001M

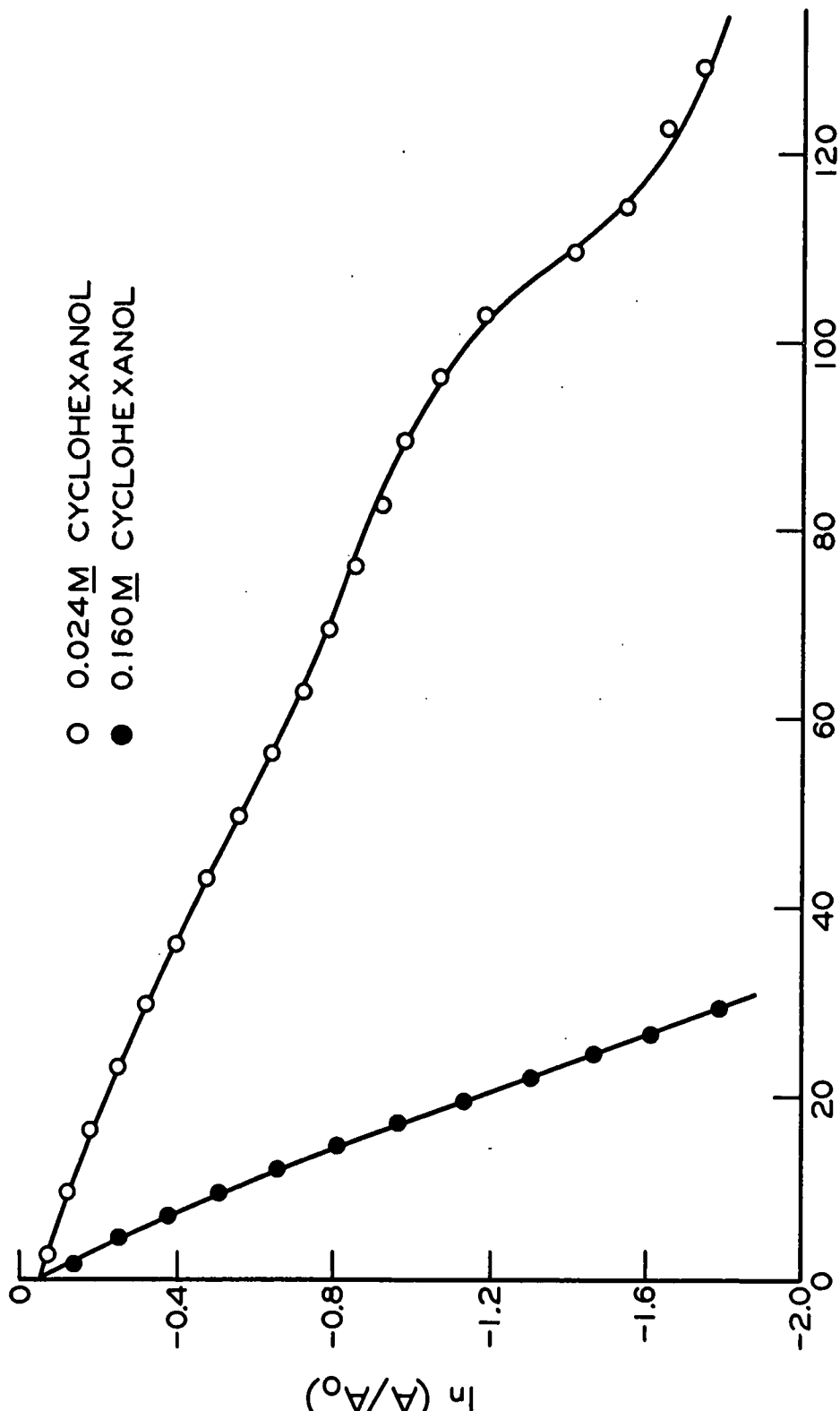


Figure 6. Reactions of Cyclohexanol in 1.0M Perchloric Acid at 15.0°C. Initial Cerium(IV) Concentration, 0.0025M

normal autocatalytic behavior is observed. However, at the lower concentrations (10-fold excess of cyclohexanol) there was an unusual oscillation in the logarithm plot. This oscillation is apparently real since it was reproduced in several cases. It appears that in this reaction something other than simple autocatalysis due to secondary oxidations is occurring.

For all reactions in which autocatalytic effects occurred, initial pseudo-first-order rate constants were calculated.

Effects of Oxygen on Reaction Kinetics

When the first experiments were carried out in 1.0M perchloric acid, it was found that the plots of the logarithm of the absorbance versus time has an unusual shape. The slope of these plots initially increased with time and finally decreased to a constant value. The middle curve in Fig. 7 illustrates this behavior. After investigating several reaction variables it was finally determined that this behavior was due to the presence of oxygen in the reaction mixture. Thus, Fig. 7 shows the effect of purging the reactant solutions with nitrogen and oxygen on reactions of trans-1,2-cyclohexanediol in 1.0M perchloric acid. When the reactants were purged with nitrogen for 30 minutes before mixing, the plot of ln A versus time was linear as expected for a pseudo-first-order reaction. Purging with oxygen, on the other hand, accentuates the deviation from linearity. To minimize the effect of dissolved oxygen the reactants for all oxidations in 1.0M perchloric acid were purged for 30 minutes with nitrogen before mixing. A similar effect of dissolved oxygen was noted in the oxidation of acetone by cerium(IV) in nitric acid solutions (88).

A series of reactions was run with 0.082M trans-1,2-cyclohexanediol in 1.0M perchloric acid and varying cerium(IV) concentrations. The results of these experiments are shown in Fig. 8. Despite the fact the reactants were purged with nitrogen

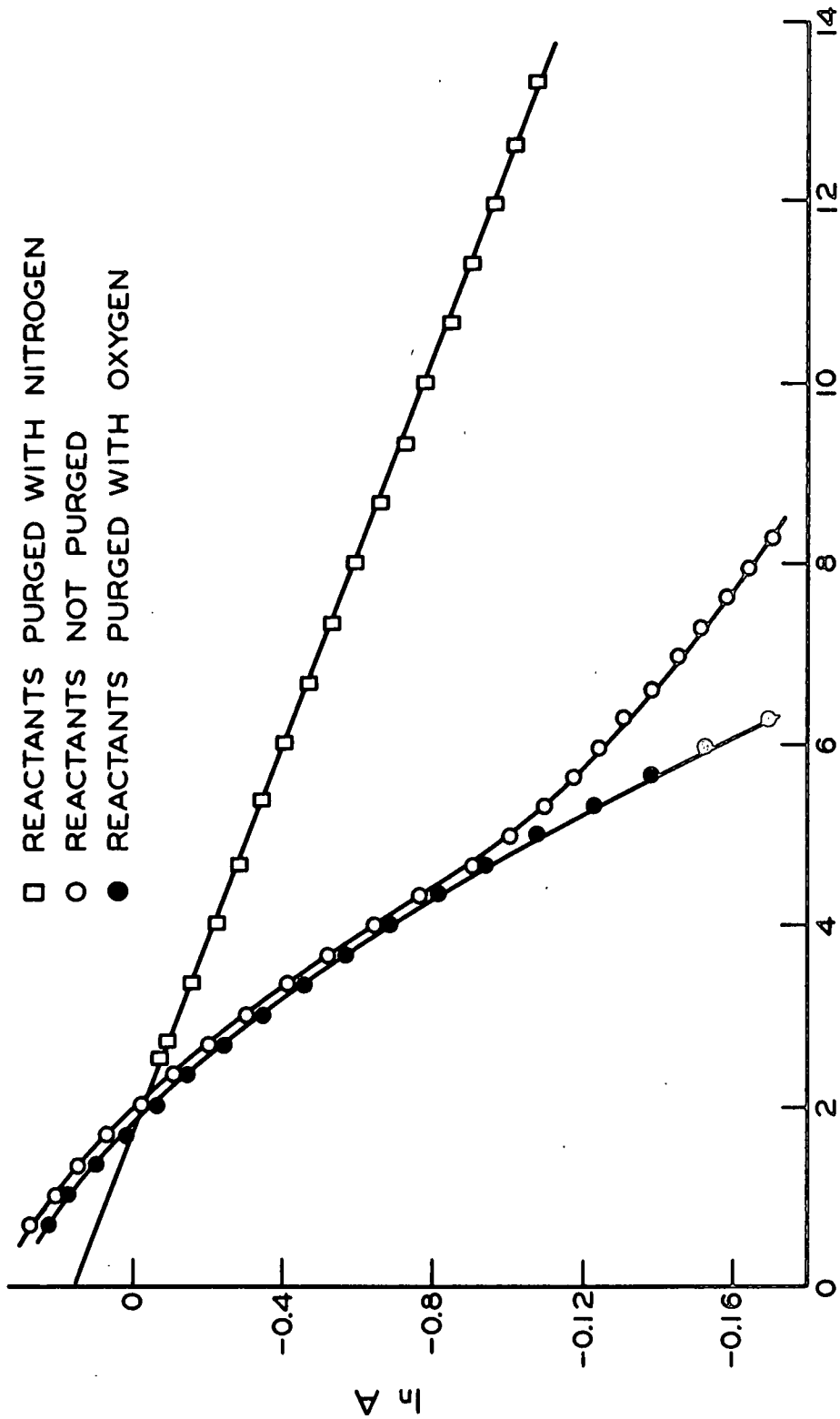


Figure 7. Effect of Oxygen on the Reaction of 0.017M trans-1,2-Cyclohexanediol in 1.0M Perchloric Acid at 15.0°C. Initial Cerium(IV) Concentration, 0.001M

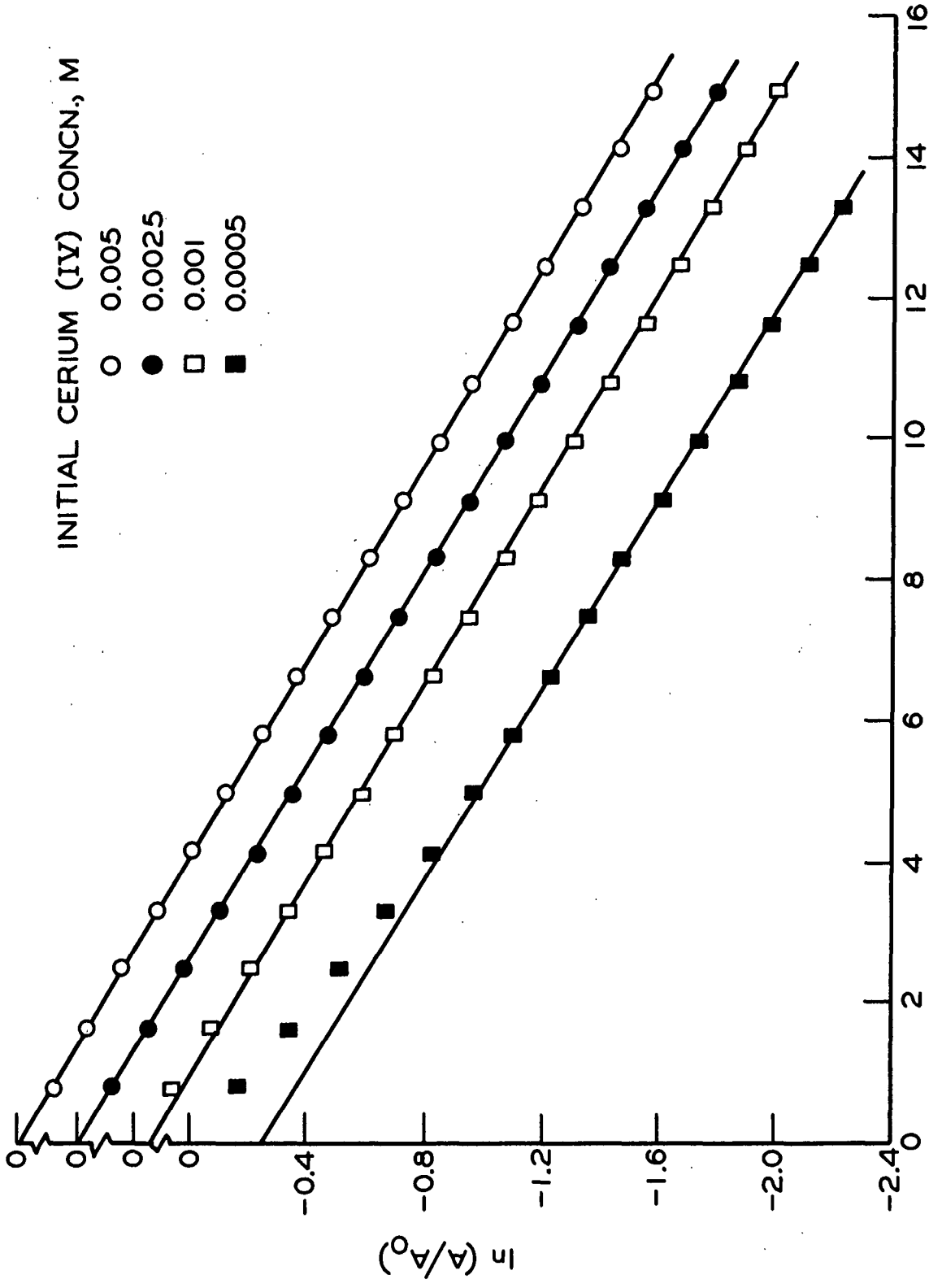


Figure 8. Effect of Initial Cerium(IV) Concentration on the Reaction of 0.082M trans-1,2-Cyclohexanediol in 1.0M Perchloric Acid at 15.0°C.

a slight initial curvature was found for the reactions at the lower initial cerium(IV) concentrations. This curvature is probably caused by traces of oxygen in the system. As the cerium(IV) concentration was increased the curvature diminished and at 0.0025M Ce(IV) the logarithm plots were entirely linear. All reactions in 1.0M perchloric acid were therefore run with 0.0025M initial cerium(IV) concentrations.

Because of its importance in reactions in 1.0M perchloric acid, the effect of oxygen was also investigated for reactions in 0.25M sulfuric and 0.75M perchloric acids. The results for cis- and trans-1,2-cyclopentanediols and trans-1,2-cyclohexanediol at 20°C. are summarized in Table VIII. The oxidations in which the reactants were nitrogen purged are all slightly faster than the ordinary reactions. However, the effect is small and opposite in direction compared to reactions in 1.0M perchloric acid. Thus, the presence of oxygen in this acid medium was not considered important. It has also been shown that the effect of oxygen is negligible in the reactions of ethylene glycol (47) and pinacol (5) in sulfuric acid media.

TABLE VIII

EFFECT OF PURGING REACTANT SOLUTIONS WITH NITROGEN FOR REACTIONS WITH 0.001M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 20°C.

Substrate	Substrate Concn., M	k', $min.^{-1}$ [a]	
		Without N_2 Purge	With N_2 Purge
cis-1,2-Cyclopentanediol	0.0200	0.114	0.119
trans-1,2-Cyclopentanediol	0.0206	0.198	0.202
trans-1,2-Cyclohexanediol	0.0399	0.000240[b]	0.000269[b]

[a] Rate constants are average of duplicate determinations. Data for individual experiments given in Table LVIII in Appendix III.
[b] Initial rate constants.

ORDER OF REACTION WITH RESPECT TO SUBSTRATE CONCENTRATION: SEARCH FOR COMPLEX FORMATION

As discussed in a previous section, determination of the dependence of the pseudo-first-order rate constant on substrate concentration provides a means for distinguishing between the various reaction mechanisms. For reactions proceeding through intermediate complexes, the pseudo-first-order rate constant is given by

$$k' = kKS/(1 + KS) \qquad (28)$$

and hence

$$1/k' = 1/k + 1/kKS \qquad (29).$$

Thus, a plot of k' versus S for these reactions will be curved, concave downward, and passing through zero. A plot of $1/k'$ versus $1/S$, however, will be linear and the equilibrium constant for complex formation, K, and the disproportionation rate constant, k, can be calculated from the slope and intercept. For the direct oxidation theory and certain variations of the complex formation theory, a plot of k' versus S will be linear with slope k_{II} and zero intercept.

Reactions in Sulfate-Containing Media

The variation of the pseudo-first-order rate constant with substrate concentration for cis- and trans-1,2-cyclopentanediols was studied in 0.5M sulfuric acid and in mixed 0.25M sulfuric and 0.75M perchloric acids. The reaction of trans-2-methoxycyclopentanol was also studied in the latter medium. The results of these experiments are shown in Fig. 9 and 10. In these graphs the averages for duplicate determinations of the pseudo-first-order rate constant are plotted versus substrate concentration. These plots are essentially linear indicating second-order kinetics, although there is a slight curvature of the type expected for reactions proceeding through intermediate complexes. The reciprocal plots ($1/k'$ versus $1/S$) for these reactions were good straight lines, but the intercepts were very close to zero.

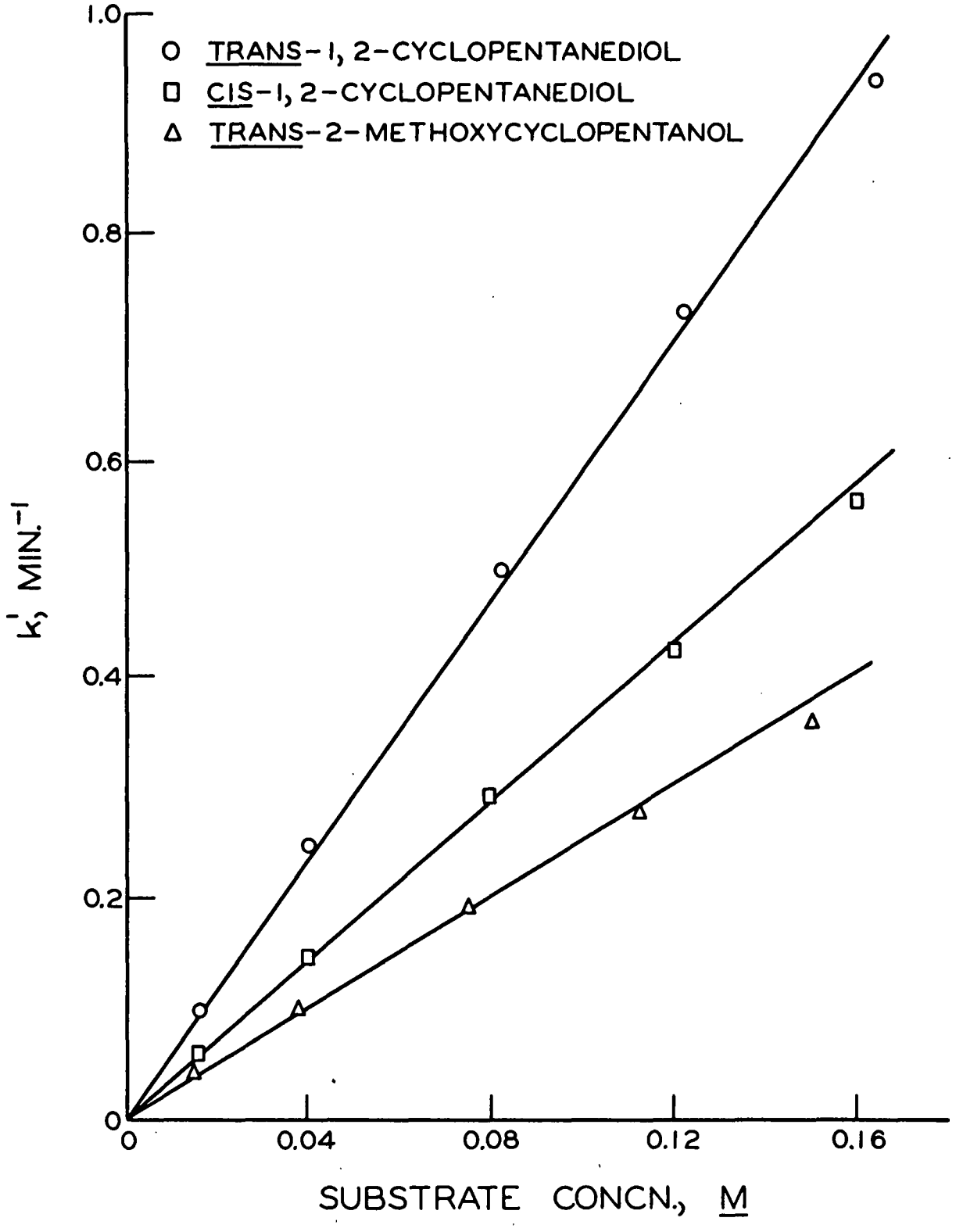


Figure 9. Effect of Substrate Concentration on the Pseudo-First-Order Rate Constant for Reactions in 0.25M Sulfuric and 0.75M Perchloric Acids at 15.0°C. Initial Cerium(IV) Concentration, 0.00025M

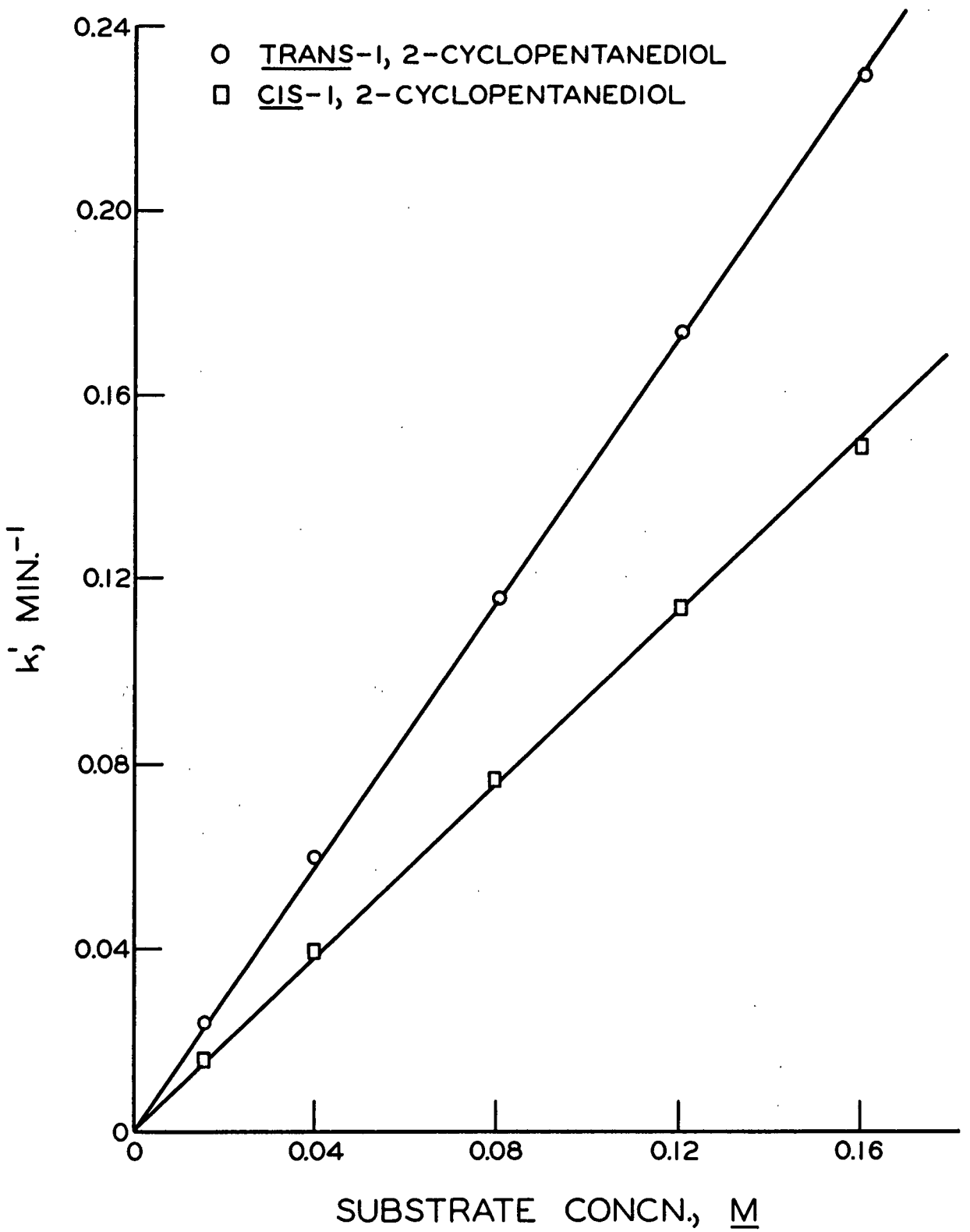


Figure 10. Effect of Substrate Concentration on the Pseudo-First-Order Rate Constant for Reactions in 0.5M Sulfuric Acid at 15.0°C. Initial Cerium(IV) Concentration, 0.001M

The fact that the intercepts are nearly zero makes the calculation of the equilibrium constants somewhat uncertain. Also, the curvature of the plots of k' versus S may possibly be due to factors other than complex formation, such as changes in the reaction environment as the concentration of the organic substrate increases. Thus, it is probably preferable to interpret this data as indicating second-order kinetics. The second-order rate constants calculated from the slopes of Fig. 9 and 10 are shown in Table IX.

TABLE IX

SECOND-ORDER RATE CONSTANTS FOR REACTIONS IN SULFATE-CONTAINING MEDIA AT 15.0°C.

Substrate	k_{II}, M^{-1} $min.^{-1}$
1. Reactions in 0.25M Sulfuric and 0.75M Perchloric Acids	
cis-1,2-Cyclopentanediol	3.46
trans-1,2-Cyclopentanediol	5.76
trans-2-Methoxycyclopentanol	2.35
2. Reactions in 0.5M Sulfuric Acid	
cis-1,2-Cyclopentanediol	0.923
trans-1,2-Cyclopentanediol	1.429

The behavior observed in these experiments appears to be somewhat typical of cerium(IV) oxidations in reaction media containing sulfate ions. As indicated in the Introduction, second-order kinetics are frequently observed for reactions in these media. Evidence for intermediate complexes has been obtained only in a few instances. It should be noted that the failure to find positive evidence for complex formation does not preclude reaction through intermediate complexes. However, if a complex is involved in the reaction, its concentration must be small compared to the total cerium(IV).

Because of the possibility that the second-order rate constant may actually be the product of an equilibrium constant and a disproportionation rate constant, it is difficult to attach mechanistic significance to these rate constants. The second-order rate constants for cis- and trans-1,2-cyclopentanediols and trans-2-methoxycyclopentanol differ only slightly. The rate constant for the trans-diol is actually larger than for the cis. This result is somewhat surprising when compared to the lead tetraacetate and periodate oxidations of the 1,2-cyclopentanediols where the cis-isomer is oxidized many times faster than the trans.

Reactions in 1.0M Perchloric Acid

Kinetic and Spectrophotometric Evidence for Complex Formation

The reactions of cis- and trans-1,2-cyclohexanediols, trans-2-methoxycyclohexanol, and cyclohexanol were studied in 1.0M perchloric acid, since it seemed more likely that definite evidence for complex formation could be obtained in this medium. The reactions of the 1,2-cyclopentanediols and 2-methoxycyclopentanol were too rapid (even at 0°C.) in 1.0M perchloric acid to be studied by ordinary kinetic methods. In Fig. 11 plots of the pseudo-first-order rate constants versus substrate concentration for reactions in this medium at 15.0°C. are shown. These plots are definite curves indicating that the reactions proceed through intermediate complexes. Reciprocal plots for these reactions are given in Fig. 12 and 13 and the equilibrium constants and disproportionation rate constants calculated from the slopes and intercepts of the reciprocal plots are shown in Table X.

When the ceric ion and substrate solutions were mixed for the reactions in 1.0M perchloric acid, an intensification of the color of the solution was observed. The ceric ion solution, which is normally yellow, becomes red-brown in the presence of the organic substrates. Ardon (29), in a study of the reaction of ethanol with cerium(IV) in perchloric acid, developed a method for relating this color change

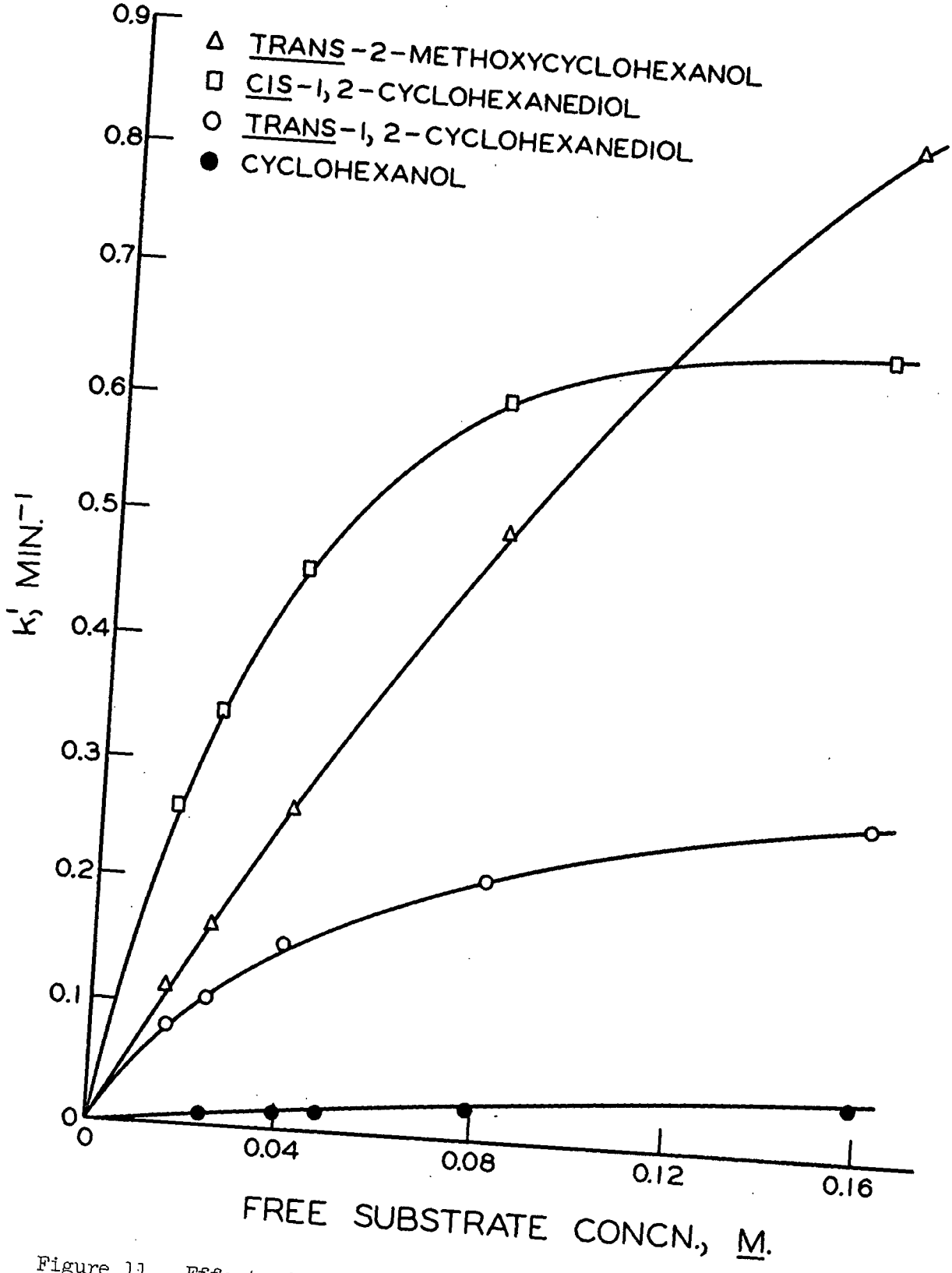


Figure 11. Effect of Substrate Concentration on the Pseudo-First-Order Rate Constant for Reaction in 1.0M Perchloric Acid at 15.0°C. Initial Cerium(IV) Concentration, 0.0025M

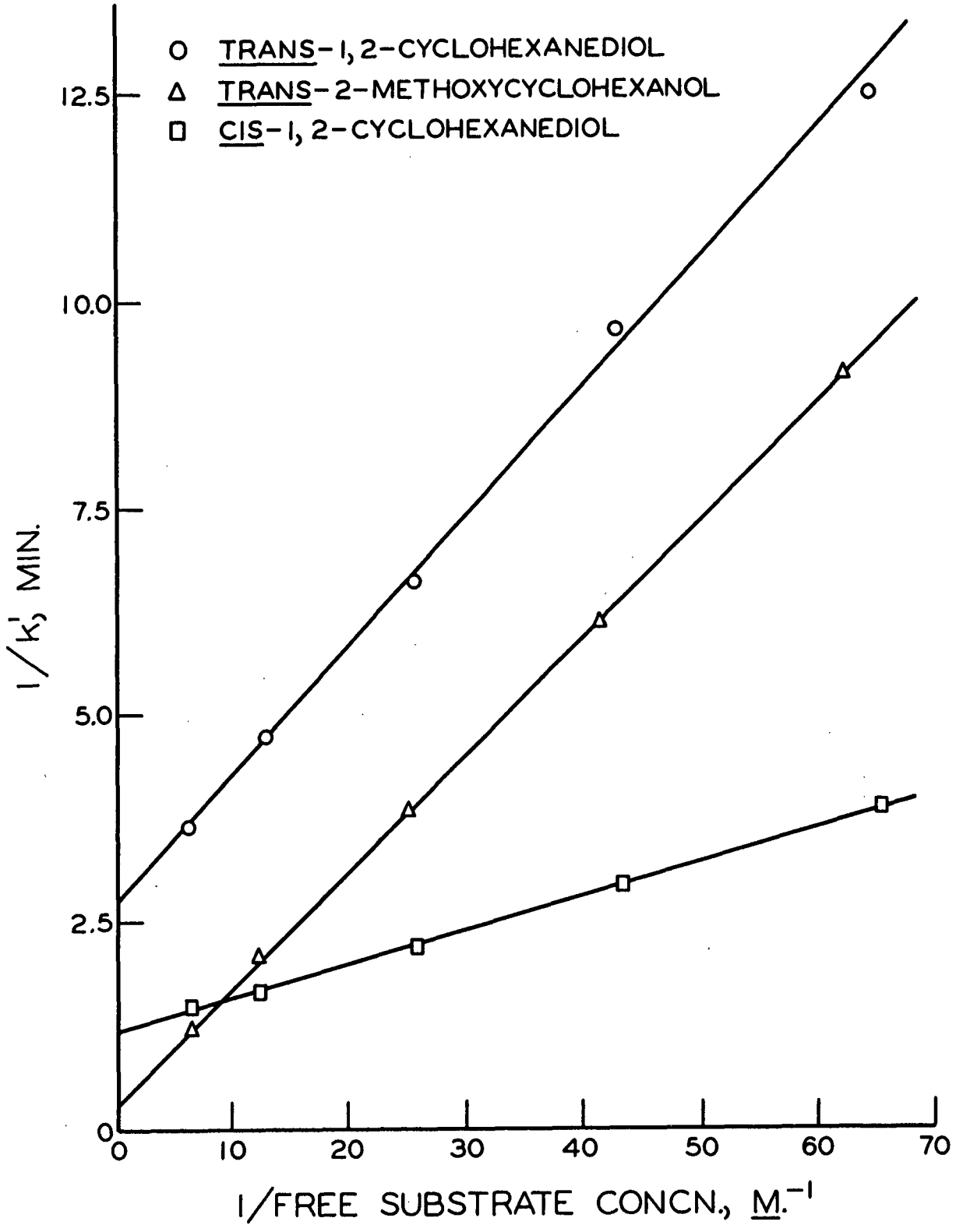


Figure 12. Reciprocal Plots for Reactions in 1.0M Perchloric Acid at 15.0°C.

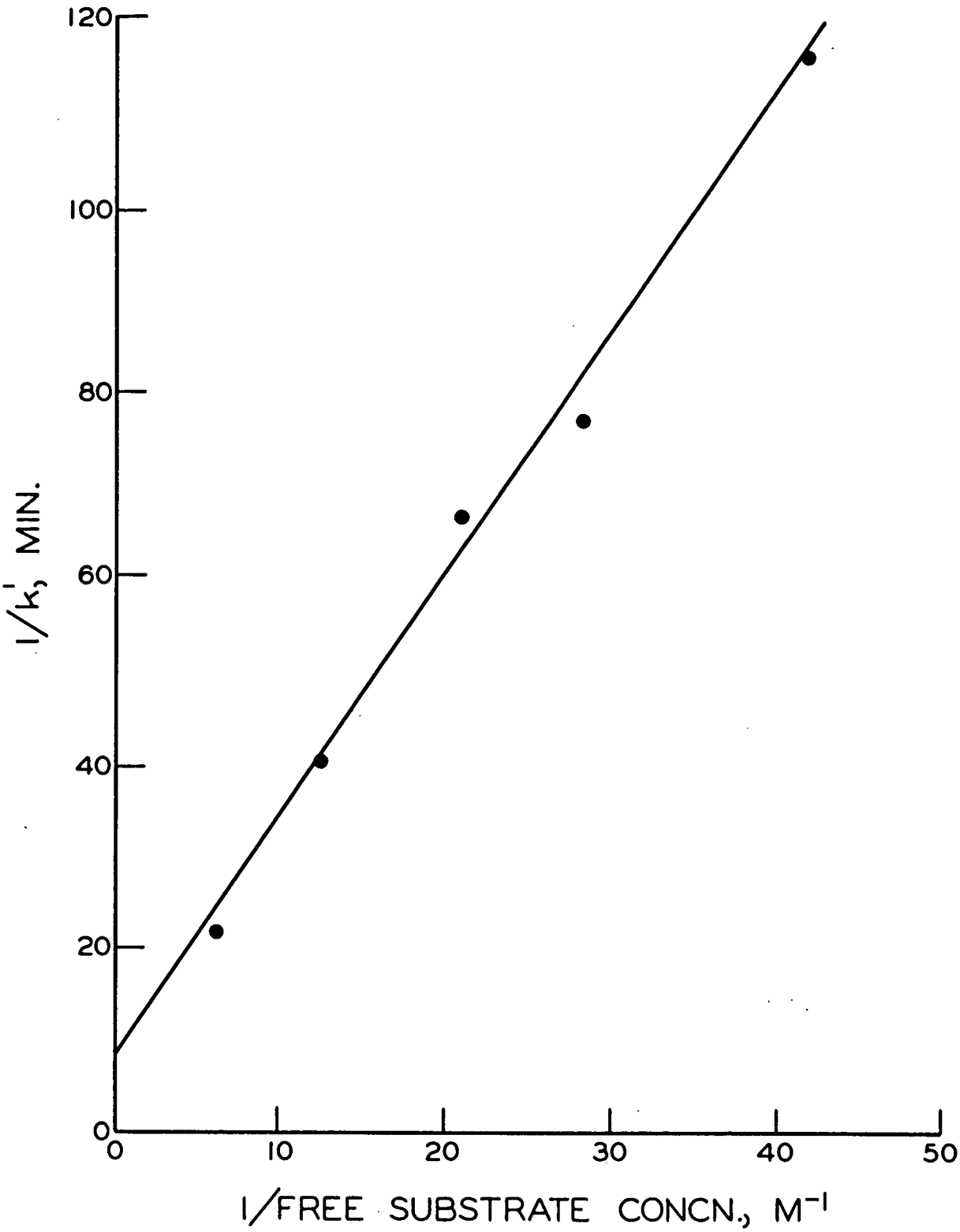


Figure 13. Reciprocal Plot for the Reaction of Cyclohexanol in 1.0M Perchloric Acid at 15.0°C.

TABLE X

EVIDENCE FOR COMPLEX FORMATION IN 1.0M PERCHLORIC ACID: COMPLEX FORMATION CONSTANTS AND RATE CONSTANTS FOR COMPLEX DISPROPORTIONATION

Substrate	Temp., °C.	Complex Formation Constant K, M^{-1}		Rate Constant k, $min.^{-1}$	Reference
		Spectrophotometric Data	Kinetic Data		
cis-1,2-Cyclohexanediol	15.0	29.3	29.0	0.85	This work
trans-1,2-Cyclohexanediol	15.0	18.6	18.0	0.36	This work
trans-2-Methoxycyclohexanol	15.0	2.9	2.1	3.3	This work
Cyclohexanol	15.0	3.9	2.9	0.13	This work
Methanol	13.0	--	2.5	0.23	(27)
	20.0	--	1.5	0.62	(27)
Ethanol	20.0	4.3	4.3	0.4	(29)
Glycerol	20.0	--	25.0	0.83	(30)

to the equilibrium constant for reactions proceeding through a 1:1 complex

$$S + Ce(IV) \underset{}{\overset{K}{\rightleftharpoons}} C \xrightarrow{k} \text{Products.}$$

If the only absorbing species in the system are complex and ceric ion, the absorbance is given by the equation

$$A = \epsilon_c C + \epsilon_{Ce}(Ce(IV) - C) \tag{30}$$

where

ϵ_c = molar absorptivity of the complex

ϵ_{Ce} = molar absorptivity of cerium(IV)

C = concentration of complex

$Ce(IV)$ = total cerium(IV) concentration.

Since

$$C = [KS/(1 + KS)]\ Ce(IV) \tag{31}$$

we have

$$A = \Delta\epsilon[KS/(1 + KS)]\ Ce(IV) + \epsilon_{Ce}Ce(IV) \tag{32}$$

and

$$A - A_b = \Delta\epsilon[KS/(1 + KS)]\ Ce(IV) \tag{33}$$

where $\Delta\epsilon = \epsilon_c - \epsilon_{Ce}$ and $A_b = \epsilon_{Ce}Ce(IV)$, i.e., the absorbance that would be observed in the absence of the organic substrate. At zero time,

$$A_o - A_b = \Delta\epsilon[KS/(1 + KS)]\ Ce(IV)_o \tag{34}$$

or

$$1/(A_o - A_b) = 1/\Delta\epsilon Ce(IV)_o + 1/\Delta\epsilon Ce(IV)_o KS \tag{35}.$$

The equilibrium constant can thus be evaluated from a reciprocal plot of $1/(A_o - A_b)$ versus $1/S$:

$$K = \text{intercept/slope.}$$

The quantity $A_o - A_b$ was therefore determined for all the reactions in 1.0M perchloric acid. A_o was found by extrapolation of the plots of the logarithm of the absorbance versus time to zero time. A_b was taken as the absorbance of a blank solution prepared in the same manner as the reaction mixture but without any substrate. The equilibrium constants were calculated from the slopes and intercepts of the reciprocal plots shown in Fig. 14 and 15.

Thus, for the reactions in 1.0M perchloric acid, evidence for complex formation was obtained by kinetic and spectrophotometric methods. The equilibrium constants for complex formation determined by the two methods are compared in Table X along with the complex disproportionation rate constant calculated from the kinetic data. Literature data for some reactions in 1.0M perchloric acid are also given. The kinetic and spectrophotometric methods are independent techniques and are subject to different types of experimental errors. The agreement in the equilibrium constants is therefore quite satisfactory.

Discussion of the Significance of Complex Formation Data

As indicated in the Introduction, cerium(IV) in aqueous perchloric acid solutions exists as a number of hydrated ionic species which may include Ce^{4+}, $CeOH^{3+}$, $Ce(OH)_2^{2+}$, and $(Ce\text{-}O\text{-}Ce)^{6+}$. The dimeric species increases with the total cerium(IV) concentration and is usually negligible at the low cerium(IV) concentrations used in kinetic studies. The hydrolysis reactions, however, are significant even at high acidities. In several studies (27, 29, 30) of cerium(IV) oxidations in perchloric acid it has been observed that the rate increases with acid concentration, indicating that the reactive cerium(IV) species is unhydrolyzed, probably hydrated Ce^{4+}.

The equilibrium constants obtained from the kinetic and spectrophotometric data are based on the total cerium(IV) concentration and are therefore apparent

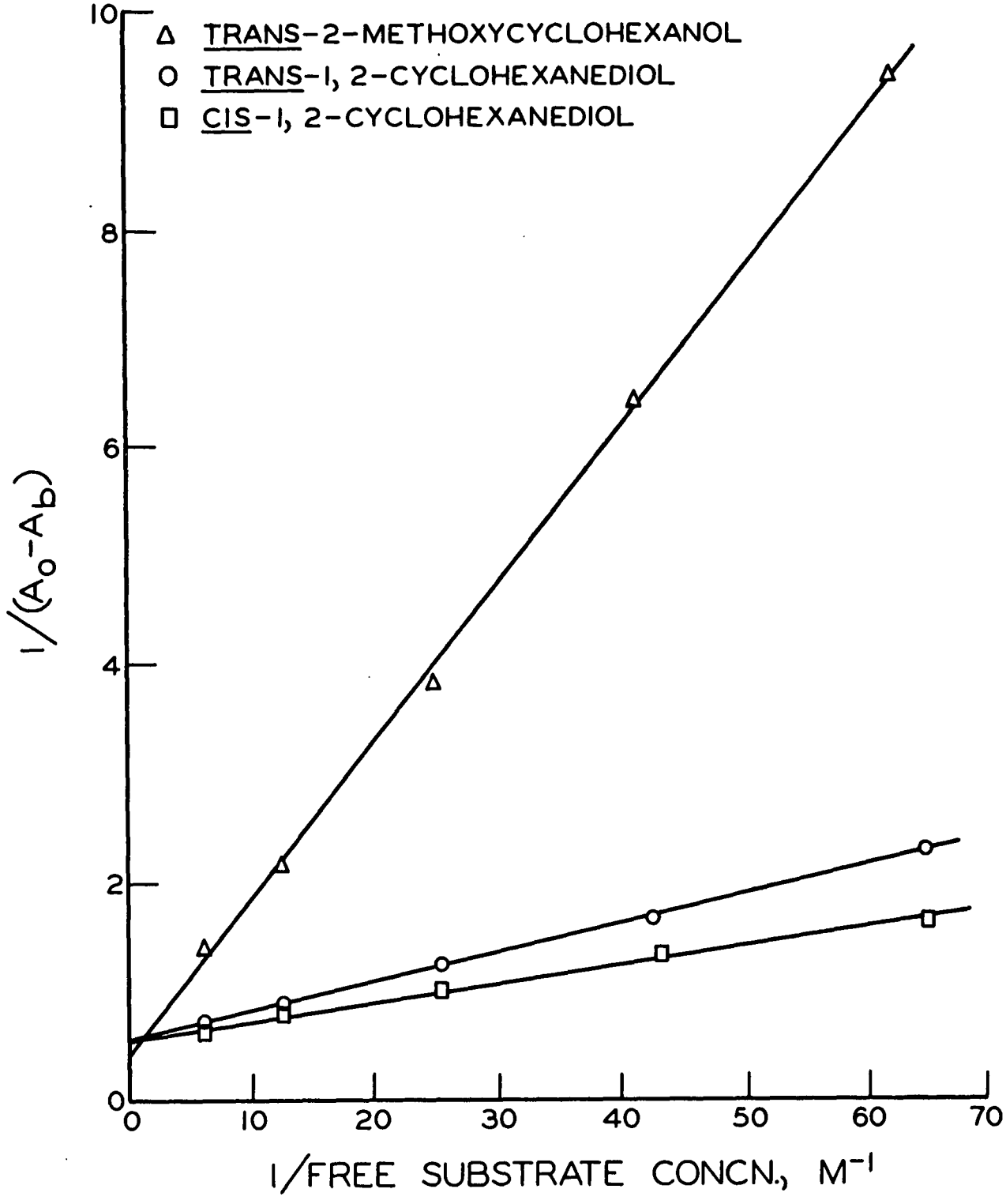


Figure 14. Reciprocal Plots of Spectrophotometric Data for Reactions in 1.0M Perchloric Acid at 425 mμ and 15.0°C.

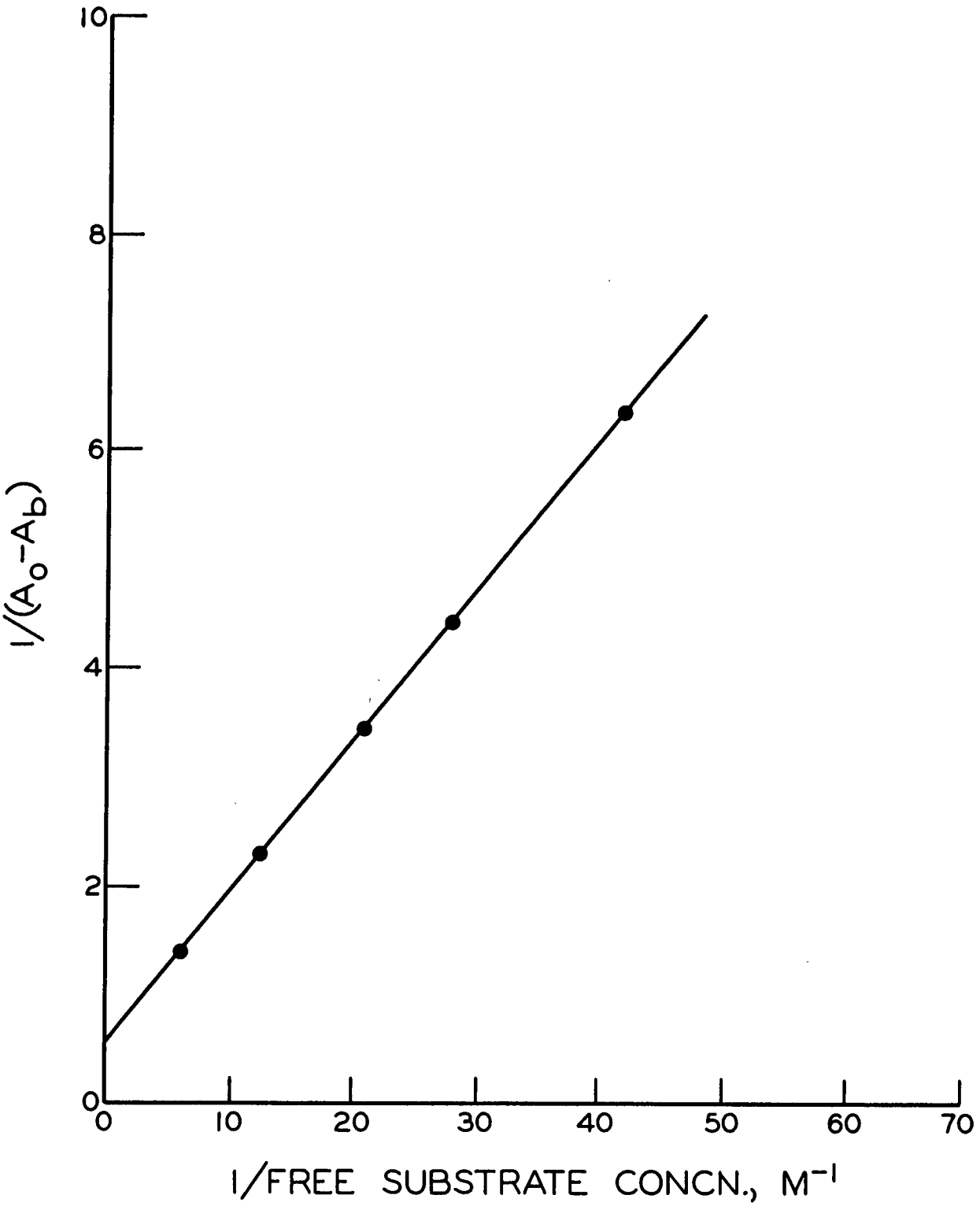


Figure 15. Reciprocal Plot of Spectrophotometric Data for the Reaction of Cyclohexanol in 1.0M Perchloric Acid at 425 mμ and 15.0°C.

equilibrium constants dependent on the concentration of acid. Assuming the hydrolysis equilibrium

$$Ce^{4+} + H_2O \overset{K_h}{\rightleftharpoons} CeOH^{3+} + H^+ \qquad (36)$$

it can be shown (27) that the true equilibrium constant, $\bar{K}$, is related to the apparent equilibrium constant, K, by the equation

$$\bar{K} = K(1 + K_h/H^+) \qquad (37)$$

$$\bar{K} = C'/Ce^{4+}S \qquad (38)$$

where

Ce^{4+} = concentration in solution of the cerium(IV) species, Ce^{4+}

C' = concentration of the Ce^{4+}-S complex.

Equation (37) has been verified experimentally by Muhammad and Rao (27) for the reaction of methanol with ceric perchlorate. It is evident from Equation (37) that under any given experimental conditions the apparent equilibrium constant differs from the true value by a constant factor. Thus, it is valid to use the apparent equilibrium constants for comparisons between various substrates, provided the experimental conditions are maintained constant.

In Table X values for the apparent equilibrium constants for reactions in 1.0M perchloric acid are summarized. The presence of adjacent hydroxyl groups in the organic substrate causes a substantial increase in the stability of the complex compared to compounds with only one hydroxyl. Thus, the equilibrium constants for cis- and trans-1,2-cyclohexanediols (29.0 and 18.0, respectively) are considerably larger than for the monohydric alcohols cyclohexanol and trans-2-methoxycyclohexanol (2.1 and 2.9, respectively). Similarly, the literature results indicate that glycerol forms a more stable complex with cerium(IV) than methanol and ethanol.

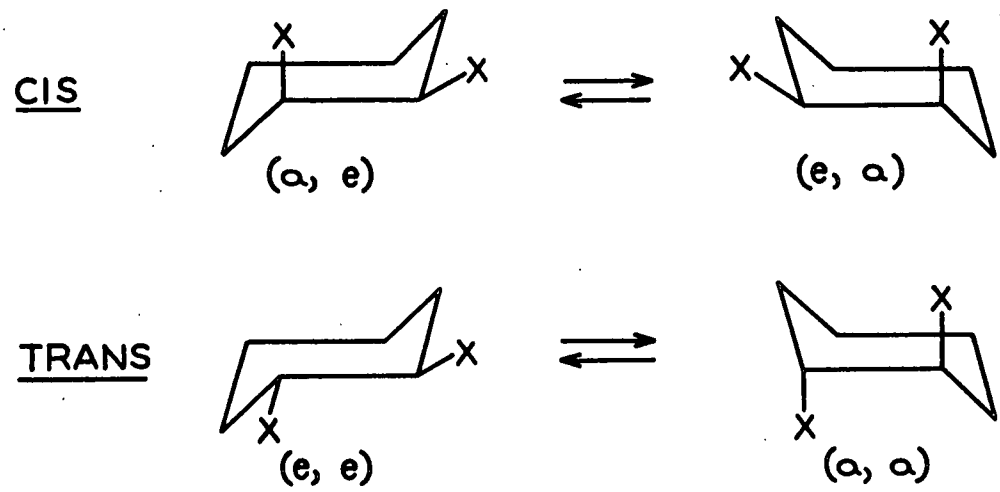
The greater stability of 1,2-glycols indicates that these compounds form a chelate complex with cerium(IV).

The large difference between the equilibrium constants for trans-1,2-cyclohexanediol and trans-2-methoxycyclohexanol and the similarity of the values for the latter compound to cyclohexanol, methanol, and ethanol suggests that trans-2-methoxycyclohexanol does not form a chelate complex with cerium(IV). The possibility of a chelate complex cannot be entirely excluded on the basis of these results, since the methoxyl group could simply reduce the stability of the chelate rather than totally prevent chelate formation. However, the results of comparisons of the entropies of activation for the cis- and trans-2-methoxycyclohexanols indicate that an acyclic complex is formed with this compound. (See section concerning the temperature dependence of cerium(IV) reactions.)

While the equilibrium constants for cis- and trans-1,2-cyclohexanediols are significantly larger than for trans-2-methoxycyclohexanol, the reverse is true for the disproportionation rate constants. The disproportionation rate constant for trans-2-methoxycyclohexanol is almost 10 times larger than for the trans-diol. The net result is that the over-all rate constants (at low substrate concentrations), $k\underline{K}$, are about the same for these two compounds. Thus, chelate formation does not appear to be a necessary requirement of the oxidation reaction. This result predicts that cerium(IV) could oxidize compounds such as trans-9,10-dihydrophenanthrene-9,10-diol and trans-9,10-decalindiol, in which chelate complex formation is difficult or impossible, at rates comparable to the corresponding cis-isomers.

The relative stabilities of chelate complexes formed by the 1,2-cyclohexanediols will depend to a large measure on the nature and conformation of the chelate ring. Studies of the conformations of cyclohexane and cyclohexane derivatives

show that these compounds exist predominantly in an essentially strain-free chair form. For 1,2-disubstituted derivatives the two configurations (cis and trans) can each exist in two conformations:



The two forms of the cis-isomer are equally stable and will be present in equal amounts. However, because of the adverse 1,3-interactions in the diaxial (a, a) conformation, the trans-isomer will be predominantly in the (e, e) form (89). The dihedral angle between 1,2-substituents of cyclohexane derivatives predicted on the basis of a perfect chair conformation is 60° for the stable trans-isomer (e, e) and both forms of the cis-isomer. The (a, a) form of the trans-isomer has a dihedral angle of 180°. Thus, the hydroxyl groups in the stable conformations of cis- and trans-1,2-cyclohexanediols are in approximately the same relative positions, although calculations based on infrared measurements of intramolecular hydrogen bonding indicate the actual dihedral angle for the cis-isomer is about 50° (56).

Even though the positions of the hydroxyl groups of cis- and trans-1,2-cyclohexanediols are approximately the same, there are important differences in the abilities of these compounds to form cyclic complexes, particularly when

complex formation requires deformation of the cyclohexane ring. When ring formation results in a nearly planar 5-membered ring fused to the cyclohexane ring, as in the formation of cyclic ketals (73, 90) and borate complexes (73, 91), the reaction occurs most readily with the cis-isomers. Formation of such rings requires a bending together of the hydroxyls to a dihedral angle considerably less than 60°. The movement together of the cis-hydroxyls would be resisted only by the potential barrier of conformer interconversion, whereas bending together of the trans-hydroxyls requires increased puckering of the ring against a relatively large potential barrier (92, 93), and thus a trans-complex will be more strained than a cis-complex.

The actual conformation preferred by a 5-membered ring chelate complex will depend on the bond lengths and bond angles of the atoms involved. As the size of the coordinating atom and hence the length of the bonds to the oxygen increase, it would be expected that the ring would assume a more puckered conformation requiring less deformation of the dihedral angle of the hydroxyls.

For the octahedral periodate dianion, $H_3IO_6^{2-}$, the distance between the adjacent oxygen atoms is 2.73 A. (94), very close to the calculated interoxygen distance in the cis- and trans-1,2-cyclohexanediols [2.86 A. (95)]. Thus, the hydroxyl-oxygens of both the cis- and trans-isomers should be able to coordinate with periodate ion with only slight changes in the dihedral angle. Experimentally, the equilibrium constant for the periodate complexes was found to be larger for the trans-isomer than the cis. The smaller value for the cis-diol was attributed to an interference between one of the oxygens of the periodate anion and the carbon of the cyclohexane ring adjacent to the glycol group (39).

Since the interoxygen distances in the periodate dianion are nearly equal to the interoxygen distances in the 1,2-cyclohexanediols, it might be predicted that complexes with central atoms larger than I^{7+} would form chelates most readily with

the trans-diol. However, the conformation of a chelate ring will depend on a number of factors, including the length of the oxygen bonds to the coordinating atom and the bond angles of all the atoms involved in the ring. Thus, the cyclic intermediate in lead tetraacetate oxidations of the 1,2-cyclohexanediols is apparently formed more easily with the cis-isomer than the trans, although the interoxygen distance in lead tetraacetate (3.6 A.)[1] is considerably larger than this distance in the diols (1.86 A.).

The situation for cerium(IV) complexes is similar to the lead(IV) case with respect to the distance between adjacent oxygen atoms coordinated to the cerium(IV). Cerium(IV) is a large ion with an ionic radius of 1.01 A. (compared to 0.84 A. for Pb^{4+} and 0.50 A. for I^{7+}). The cerium(IV)-oxygen bonds are therefore quite long (2.4 A.)[2] and the calculated interoxygen distance for an octahedral complex is 3.4 A. While distribution experiments with ceric nitrate indicate a coordination number of six (97), the formation of chelate complexes with four acetylacetone ligands suggests a coordination number of eight, provided all donor atoms participate in the complex (98). The interoxygen distance in a cerium(IV) complex with eight coordination number would depend on the particular configuration of the complex, but could be considerably less than the 3.4 A. calculated for sixfold coordination. Scale models[3] were made of the complex of cerium(IV) with cis- and trans-1,2-cyclohexanediols assuming sixfold coordination with 2.4 A. cerium-oxygen bonds. The models can be made with almost equal ease for both the cis and trans-isomers. The five-membered chelate ring formed with both isomers is in a half-chair puckered conformation and in both cases involves considerable angle

---

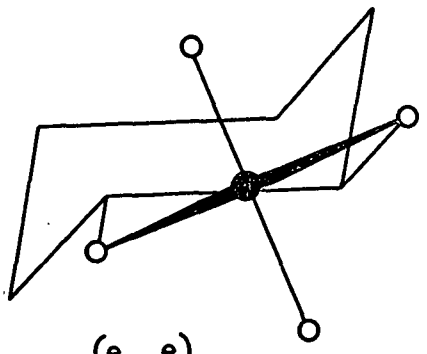
[1] Calculated assuming tetrahedral coordination and 2.2 A. Pb-O bond [sum of ionic radii for Pb^{4+} and O^{2-} (96)]. For octahedral coordination the calculated interoxygen distance is 3.1 A.

[2] Calculated from the sum of ionic radii for Ce^{4+} and O^{2-} (96).

[3] Cenco Petersen Molecular Models.

strain. Internal steric repulsions of the type suggested for the periodate-cis-1,2-cyclohexanediol complex (39) do not appear to be important in the model for the cerium(IV)-cis-diol complex. On the basis of these models then, it would appear that cerium(IV) would form almost equally stable complexes with cis- and trans-1,2-cyclohexanediols. Experimentally, it was found that the complex with cis-diol is somewhat more stable (K_{cis} = 29.0; K_{trans} = 18.0) indicating that the formation of the chelate complex may require some distortion of the hydroxyls of the diol toward coplanarity. The failure of the scale models to predict this result may be related to the assumption of an octahedral configuration for the complex.

There is one difference between the cerium(IV) chelate complexes with the cis- and trans-isomers of 1,2-cyclohexanediol that may contribute to the greater stability of the cis-isomer. Formation of chelate complexes with the trans-diol can occur only with the diequatorial conformer, (e, e), and the complex is a relatively rigid structure restricted to a single conformation as shown in the following figure*:

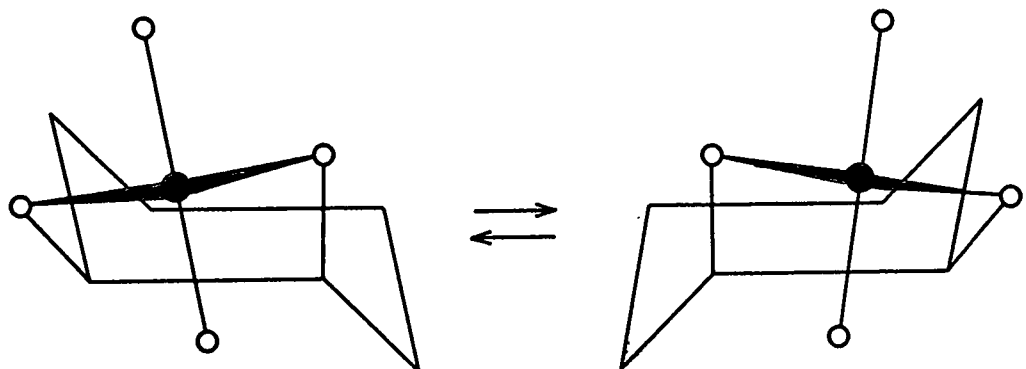


(e, e)

On the other hand, the cerium(IV) chelate complex can form with both conformations of the cis-diol [(a, e) and (e, a)]. Furthermore, interconversion between the two

*In these diagrams octahedral coordination of the cerium(IV) is assumed although for clarity the bonds to two of the ligands (water molecules or hydroxyl ions) are not shown.

chair forms of the cyclohexane rings can occur as readily in the complex as in the uncoordinated diol:



The chelate complex with the cis-diol is thus a somewhat more flexible structure. This greater flexibility should contribute to a more positive entropy change for formation of the cis-isomer chelate and therefore increase the stability of the cis-complex relative to the trans.

EFFECT OF SULFATE ION CONCENTRATION

The reactions of cis- and trans-1,2-cyclopentanediols were studied in a series of solutions with total sulfate ion concentrations varying from 0.25M to 0.75M. Since the second ionization constant of sulfuric acid is small, essentially all the sulfate ions were present as bisulfate ions (99). The hydrogen ion concentration was 1.0N and the molar ionic strength 1.0. The results of these experiments are summarized in Fig. 16 and in Table XI. The rate constants for these reactions were found to increase with decreasing total sulfate concentration indicating that the less sulfated cerium(IV) species are more effective oxidants. This result is entirely reasonable since incorporation of sulfate ions into the coordination sphere of cerium(IV) (in place of water molecules) reduces the effective positive charge of the cerium(IV) and hence its electrophilic attraction for the reductant molecules.

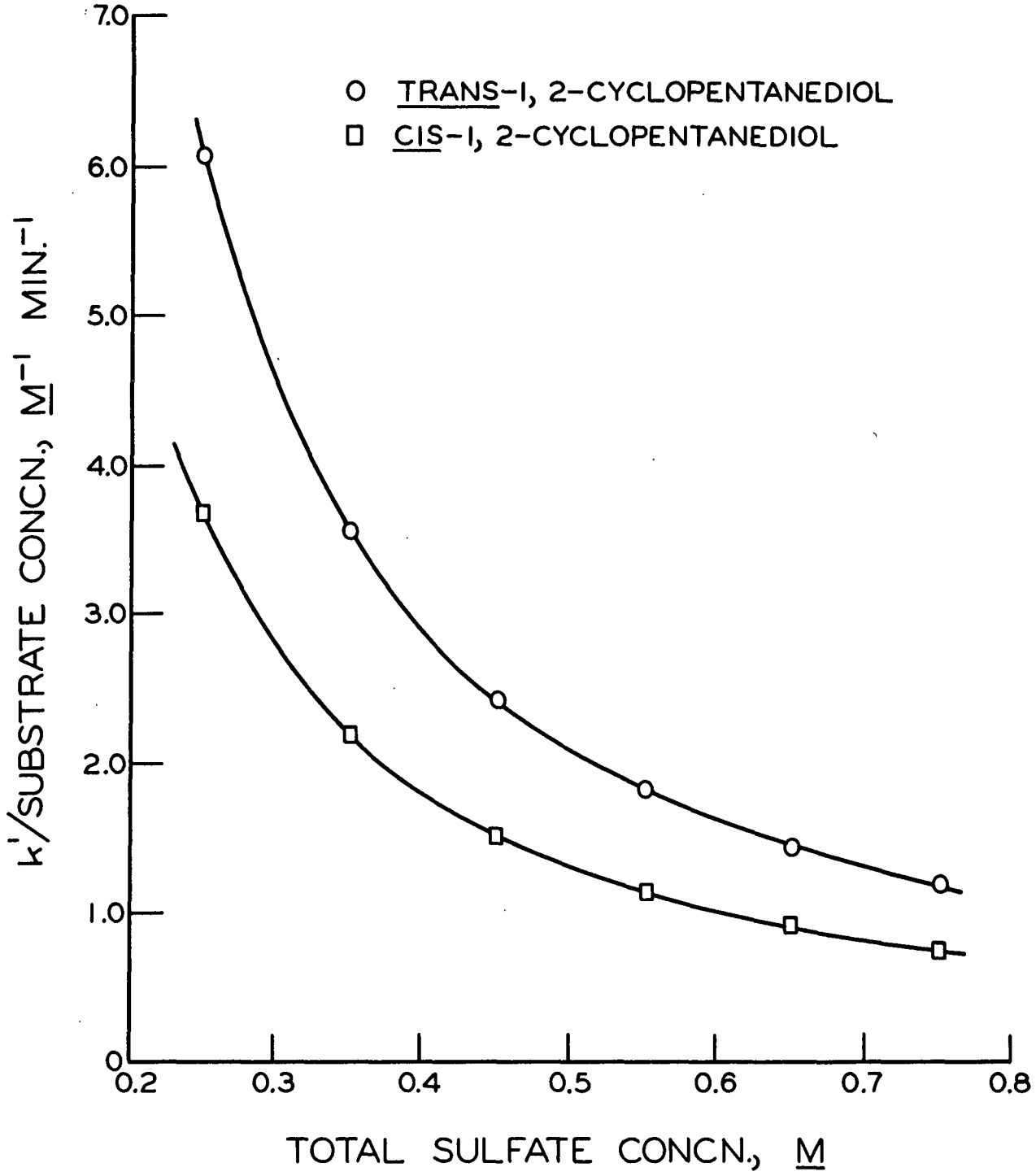


Figure 16. Effect of Total Sulfate Ion Concentration on the Reactions of cis- and trans-1,2-Cyclopentanediols at 15.0°C. Initial Cerium(IV) Concentration, 0.00025M; Hydrogen Ion Concentration, 1.0N

TABLE XI

EFFECT OF TOTAL SULFATE ION CONCENTRATION ON THE REACTIONS OF *cis*- AND *trans*-1,2-CYCLOPENTANEDIOLS AT 15.0°C.

Concentrations, M		Rate Constants[a]		
H_2SO_4	$HClO_4$	cis	trans	trans/cis
0.25	0.75	3.68	6.07	1.65
0.35	0.65	2.18	3.56	1.63
0.45	0.55	1.52	2.43	1.60
0.55	0.45	1.15	1.83	1.59
0.65	0.35	0.916	1.43	1.56
0.75	0.25	0.761	1.20	1.58

[a]Average values of apparent second-order rate constants (k'/substrate concentration), units: liter $mole^{-1}$ $min.^{-1}$.

The ratio of the oxidation rates for *cis*- and *trans*-1,2-cyclopentanediols was found to vary little over the range of sulfate ion concentrations studied (see Table XI). This result suggests that there may be only one active oxidant species or, if more than one species are involved, the relative rates of oxidation of the *cis*- and *trans*-isomers by the several species are similar.

Hardwick and Robertson (18) found that cerium(IV) solutions contain varying amounts of hydrated Ce^{4+}, $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$ and determined equilibrium constants for the equilibria:

$$Ce^{4+} + HSO_4^- \underset{}{\overset{K_1}{\rightleftharpoons}} CeSO_4^{2+} + H^+$$

$$CeSO_4^{2+} + HSO_4^- \overset{K_2}{\rightleftharpoons} Ce(SO_4)_2 + H^+$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} Ce(SO_4)_3^{2-} + H^+.$$

The data given by these workers were used to calculate the relative amounts of the various cerium(IV) species as a function of the total sulfate concentration (see

Fig. 17). In the range of concentrations used in this work the di- and trisulfated cerium(IV) species predominate. The percentage of $CeSO_4^{2+}$ varies from 0.33% at 0.25M sulfuric acid to 0.04% at 0.75M sulfuric acid. The concentration of the Ce^{4+} species is negligible in this concentration range (<0.0005%).

The effect of total sulfate concentration on cerium (IV) oxidations of organic compounds has been investigated by several workers. El-Tantawy and Rechnitz (50), in a study of the oxidation of oxalate by cerium(IV), considered only the equilibrium between $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$ and assumed that $Ce(SO_4)_2$ is the reactive complex. $CeSO_4^{2+}$ was assumed to be the oxidizing species in the reaction of glycerol (30), and the results of a recent study of the oxidation of glycolic acid indicated that $CeSO_4^{2+}$ is the active species in this reaction (100). On the other hand, Katai, et al. (47) suggested that all four cerium(IV) species may oxidize the organic substrate.

The assumption of any particular cerium(IV)-sulfate complex or complexes as the reactive species implies a certain dependence of the reaction rate on the total sulfate concentration. The nature of the oxidant species and rate constants for reaction with these species can then be evaluated by comparison of the experimental data with the predicted rate expression. In order to determine the reactive oxidant species in the oxidation reaction the rate expressions corresponding to various assumptions of the active cerium(IV)-sulfate complex or complexes were derived. The experimentally observed dependence on sulfate ion concentration was then compared to various predicted rate expressions. For the reactions of cis- and trans-1,2-cyclopentanediols the assumption of a single cerium(IV) species as the active oxidant was found to be inadequate. Similarly, the rate expressions predicted for reaction schemes in which any two cerium(IV)-sulfate complexes were considered the active species were not consistent with the experimental data.

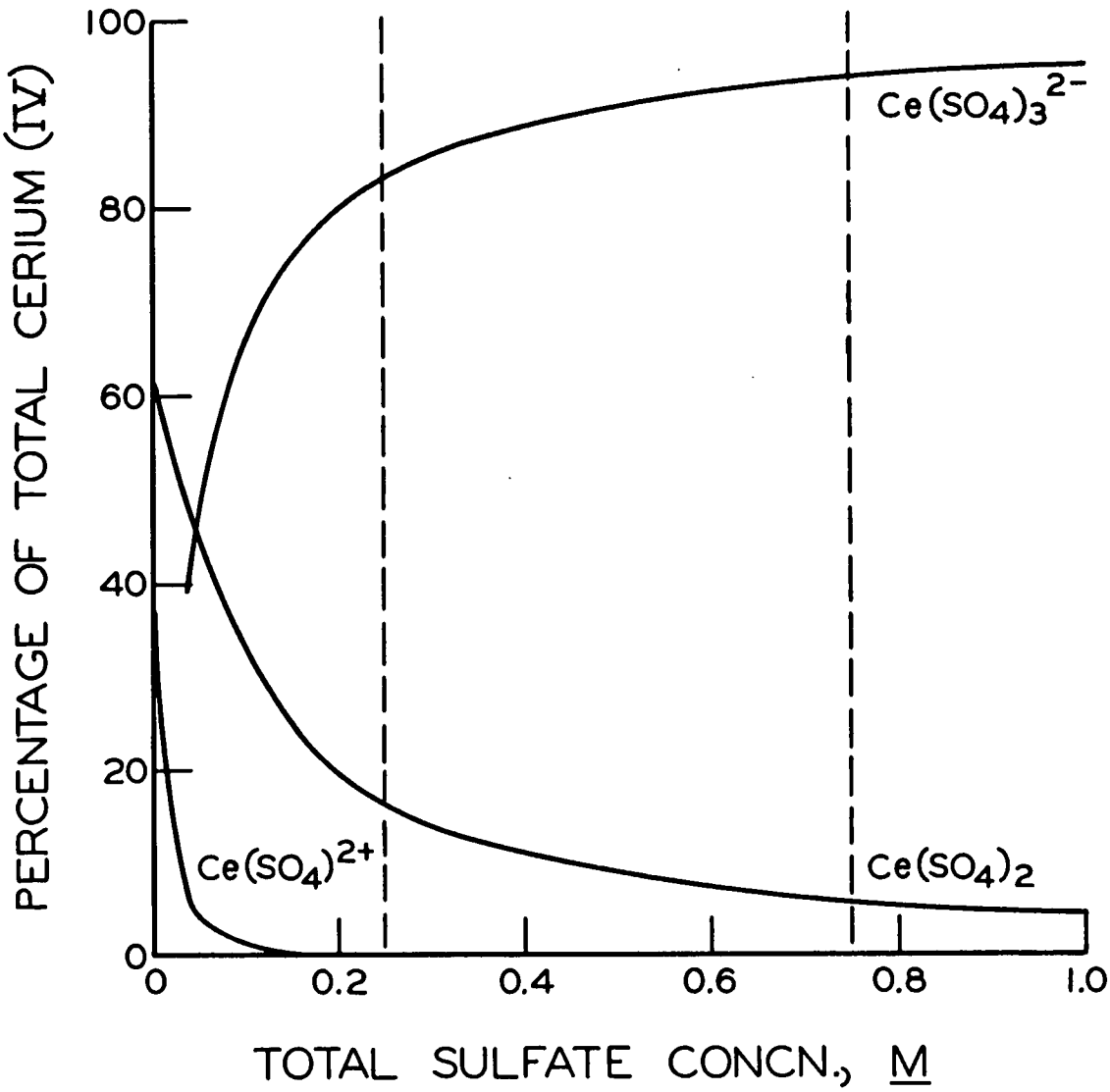


Figure 17. Variation in Percentage of Cerium(IV)-Sulfate Complexes as a Function of Total Sulfate Concentration (18). Dotted Lines Define Region Used in this Work

The observed variation in the rate constant with total sulfate concentration could be accounted for qualitatively by the reaction scheme proposed by Katai, et al. However, because of the complexity of the theoretical rate expression, individual rate constants for reactions with each of the four cerium(IV) species could not be calculated.

The reaction scheme proposed by Katai, et al. is unnecessarily general for the experimental conditions used in this work. Thus, in the range of total sulfate concentration from 0.25M to 0.75M the Ce^{4+} ion constitutes less than 0.0005% of the total cerium(IV) and even if the rate constant for reaction with this species was very large it would not be expected to contribute significantly to the reaction. It was assumed therefore that $CeSO_4^{2+}$, $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$ are the reactive species and oxidize the organic substrates through intermediate complexes.

$$CeSO_4^{2+} + S \underset{}{\overset{K_1'}{\rightleftharpoons}} C_1 \xrightarrow{k_1} \text{Products}$$

$$Ce(SO_4)_2 + S \overset{K_2'}{\rightleftharpoons} C_2 \xrightarrow{k_2} \text{Products}$$

$$Ce(SO_4)_3^{2-} + S \overset{K_3'}{\rightleftharpoons} C_3 \xrightarrow{k_3} \text{Products.}$$

In the presence of excess substrate this reaction system predicts pseudo-first-order kinetics

$$-dCe(IV)/dt = k'Ce(IV)$$

where Ce(IV) is the total cerium(IV) concentration and

$$k' = \frac{S\left[\dfrac{k_1K_1' + k_2K_2'K_2(HSO_4^-/H^+) + k_3K_3'K_2K_3(HSO_4^-/H^+)^2}{1 + K_2(HSO_4^-/H^+) + K_2K_3(HSO_4^-/H^+)^2}\right]}{1 + S\left[\dfrac{K_1' + K_2'K_2(HSO_4^-/H^+) + K_3'K_2K_3(HSO_4^-/H^+)^2}{1 + K_2(HSO_4^-/H^+) + K_2K_3(HSO_4^-/H^+)^2}\right]} \qquad (39).$$

Since experimentally the pseudo-first-order rate constant was found to be a linear function of substrate concentration it follows that

$$1 \gg S \left[\frac{K_1' + K_2'K_2(HSO_4^-/H^+) + K_3'K_2K_3(HSO_4^-/H^+)^2}{1 + K_2(HSO_4^-/H^+) + K_2K_3(HSO_4^-/H^+)^2} \right]$$

and hence the expression for the k' simplifies to

$$k' = S \left[\frac{k_1K_1' + k_2K_2'K_2(HSO_4^-/H^+) + k_3K_3'K_2K_3(HSO_4^-/H^+)^2}{1 + K_2(HSO_4^-/H^+) + K_2K_3(HSO_4^-/H^+)^2} \right] \quad (40).$$

This equation may be rearranged to

$$(k'/S)\,[1 + K_2(HSO_4^-/H^+) + K_2K_3(HSO_4^-/H^+)^2] = k_1K_1' + k_2K_2'K_2(HSO_4^-/H^+) + k_3K_3'K_2K_3(HSO_4^-/H^+)^2 \quad (41).$$

The left-hand side of Equation (41) can be evaluated from the experimentally determined apparent second-order rate constants, k'/S, and the known equilibrium constants and concentrations of bisulfate and hydrogen ion. If the assumed reaction scheme is correct, this quantity will be a quadratic function of HSO_4^-/H^+. Using multiple regression techniques it was found that a quadratic equation fit the experimental data very well with correlation coefficients exceeding 0.99. From the regression coefficients, values of the terms k_iK_i' were calculated using Hardwick and Robertson's data for K_2 and K_3. It should be noted that Hardwick and Robertson's values for the equilibrium constants for the cerium(IV)-sulfate complexes were obtained under slightly different experimental conditions. These calculations are thus approximate although it is felt that the observed trends are real.

The products k_i/K_i' can be interpreted as the over-all second-order rate constant for reaction with the cerium(IV)-sulfate complex containing i sulfate

ligands. As shown in Table XII these rate constants increase significantly as the number of sulfate ions in the complex decreases. Because of its large rate constant the $CeSO_4^{2+}$ ion accounts for a major portion of the reaction with the 1,2-cyclopentanediols, despite the fact that it is present in only small amounts [0.04 to 0.33% of the total cerium(IV)]. The calculated per cent contributions of $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$ to the oxidation reaction are shown in Fig. 18 for cis-1,2-cyclopentanediol. (The results for trans-1,2-cyclopentanediol are very similar.)

TABLE XII

RATE CONSTANTS FOR REACTION WITH INDIVIDUAL CERIUM(IV)-SULFATE COMPLEXES

	Rate Constants, M^{-1} $min.^{-1}$		
	$CeSO_4^{2+}$	$Ce(SO_4)_2$	$Ce(SO_4)_3^{2-}$
trans-1,2-Cyclopentanediol	1500	5.4	0.24
cis-1,2-Cyclopentanediol	850	4.6	0.12

In the above derivation it was assumed that the reaction proceeds by disproportionation of a complex formed in a prior equilibrium. It was shown previously that it is not possible to distinguish between this type of mechanism and a direct bimolecular oxidation reaction. If the latter mechanism is assumed, the equation derived for the variation of the pseudo-first-order rate constant with bisulfate concentration [Equation (41)] will be the same except that the products $k_{-1}K'_{-1}$ will be replaced by specific second-order rate constants.

TEMPERATURE DEPENDENCE OF THE CERIUM(IV) OXIDATION REACTION

The temperature dependence of the cerium(IV) oxidation reaction was studied for a series of nine cyclic alcohols in 0.25M sulfuric and 0.75M perchloric acids. It was expected that evidence concerning the nature of the reaction intermediate

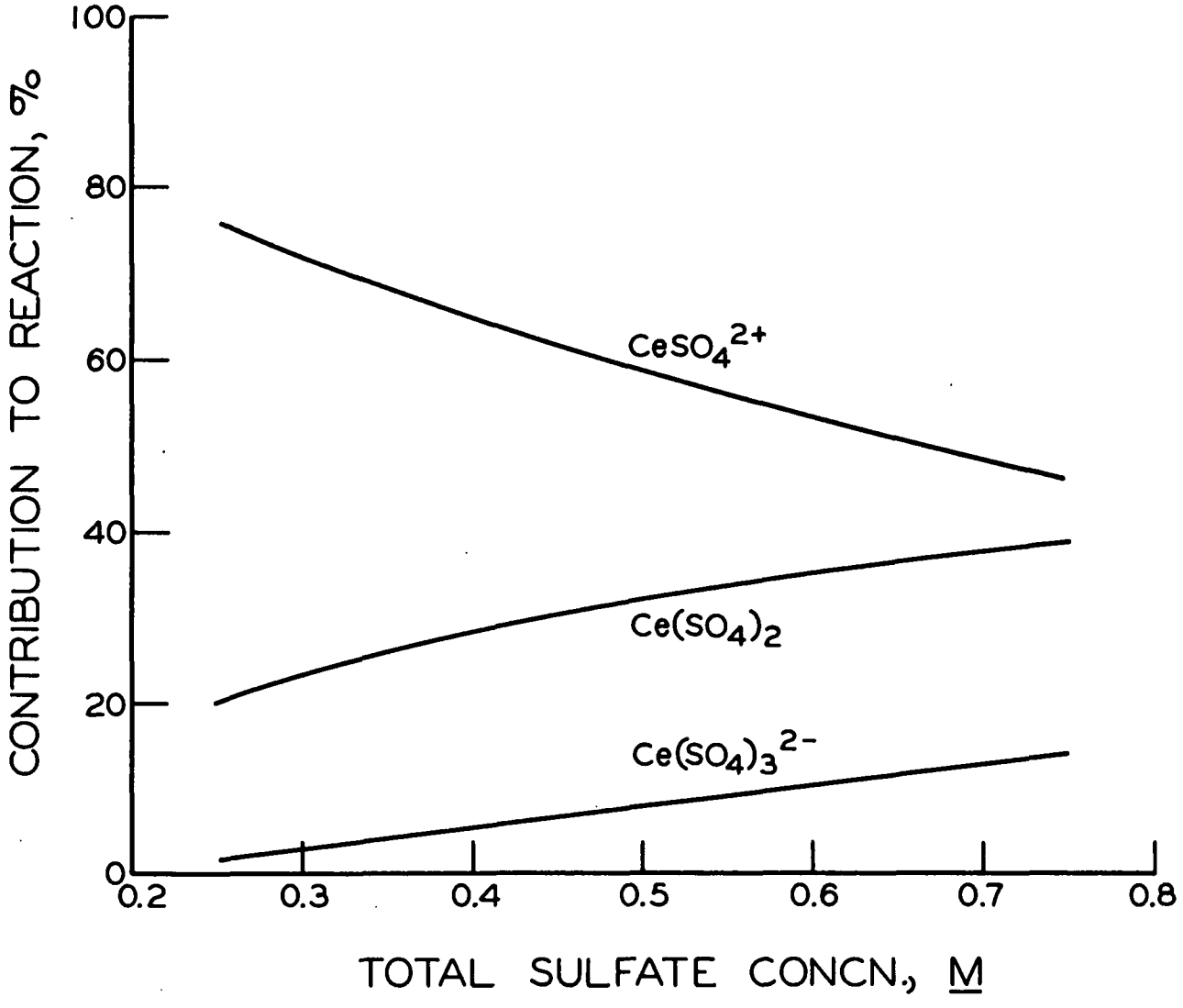


Figure 18. Calculated Contributions of Cerium(IV)-Sulfate Complexes to the Reaction of cis-1,2-Cyclopentanediol

in the oxidation could be obtained from comparisons of the entropies of activation and activation energies of these compounds. With possible exception of cyclohexanol all reactions exhibited Arrhenius temperature dependence as shown in Fig. 19 and 20. The calculated* energies and entropies of activation are given in Table XIII.

TABLE XIII

THERMODYNAMIC DATA AND RELATIVE RATES FOR REACTIONS IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS

Substrate	Relative Rate Constants (30°C.)	E_a, kcal. $mole^{-1}$	$\Delta S^{\ddagger}$, cal. $mole^{-1}$ $deg.^{-1}$
Cyclopentanol	1.0	27.5	16.5
cis-1,2-Cyclopentanediol	400	23.3	14.7
trans-1,2-Cyclopentanediol	641	23.2	15.4
trans-2-Methoxycyclopentanol	293	23.0	13.0
Cyclohexanol	(0.2)[a]	(15.2)[a]	(-27.3)[a]
cis-1,2-Cyclohexanediol	1.5	29.2	23.0
trans-1,2-Cyclohexanediol	0.46	28.0	16.6
cis-2-Methoxycyclohexanol	2.0	28.9	22.8
trans-2-Methoxycyclohexanol	0.52	30.7	25.8

[a]The accuracy of the results for cyclohexanol is questionable due to lack of precision in the duplicate rate determinations. See Fig. 20 and Table LV (Appendix III).

In the reaction of cyclohexanol in this medium the agreement between the duplicate determinations of the rate constant was quite poor. In Fig. 20 the average value of the two runs is plotted and range indicated by a vertical line

*Details of these calculations are discussed in the Experimental Section.

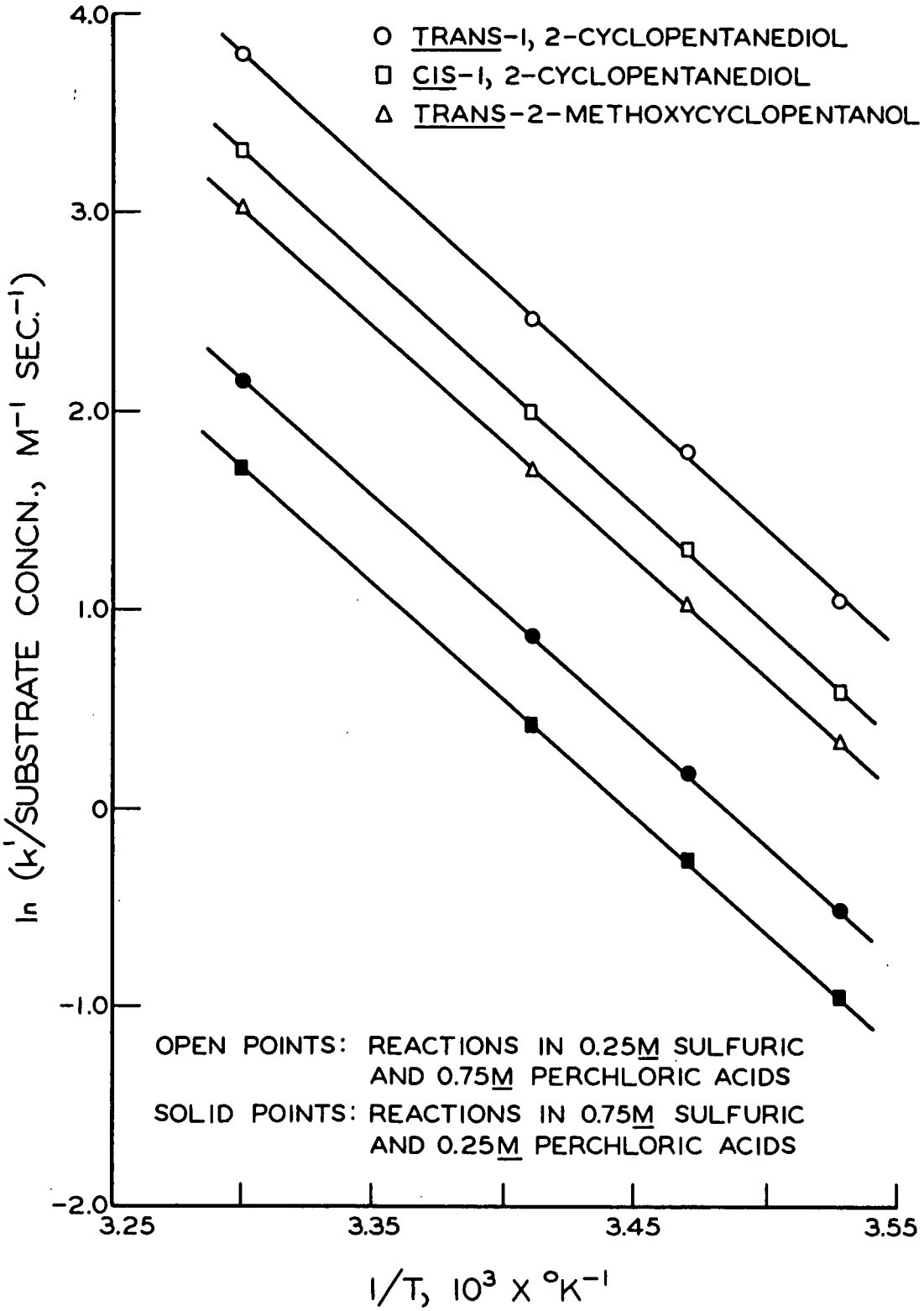


Figure 19. Arrhenius Correlations

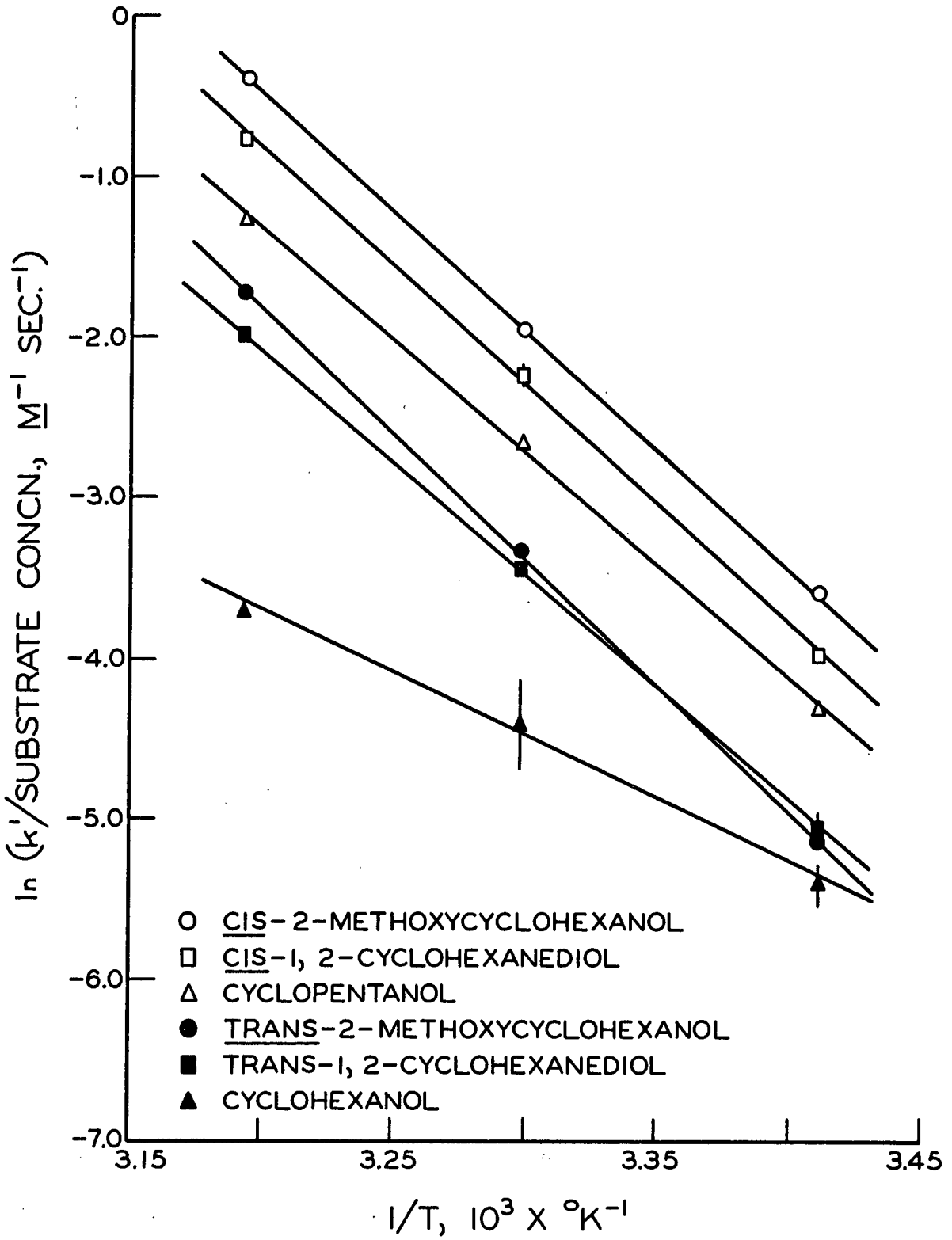


Figure 20. Arrhenius Correlations for Reactions in 0.25M Sulfuric and 0.75M Perchloric Acids

through the data points. The problem in this reaction is probably related to unusually severe autocatalysis. It is possible that the oxidation of the initial product, cyclohexanone, contributes significantly to the over-all rate even in the early portions of the reaction. The thermodynamic data calculated for this compound are therefore not considered significant.

Significance of the Activation Data

The equations used to calculate the energies and entropies of activation are strictly applicable only to the variation with temperature of a single rate constant. It was shown in the previous section that the three cerium(IV) complexes, $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$ all contribute to the oxidation reaction. From Equation (40) it follows that the apparent second-order rate constant, $\underline{k}_{II} = \underline{k}'/\underline{S}$, for cerium(IV) oxidations in sulfuric acid containing media is:

$$k_{II} = \frac{k_1 K_1' + k_2 K_2' K_2 (HSO_4^-/H^+) + k_3 K_3' K_2 K_3 (HSO_4^-/H^+)^2}{1 + K_2 (HSO_4^-/H^+) + K_2 K_3 (HSO_4^-/H^+)^2} \qquad (42).$$

The three terms in the numerator of Equation (42) represent the contributions of each of the three reactive oxidant species to the reaction. Each term is the product of a specific rate constant and one or more equilibrium constants. The over-all temperature dependence of $\underline{k}_{II}$ will thus reflect the temperature dependence of all of these rate and equilibrium constants. It is necessary, therefore, to consider the significance of the observed Arrhenius temperature dependence and of the calculated thermodynamic functions.

It can be shown (101) that Arrhenius temperature dependence should be observed for reactions in which the over-all rate constant is the product of a rate constant and one or more equilibrium constants. For a reaction involving a prior equilibrium

$$A + B \underset{}{\overset{K}{\rightleftharpoons}} C \xrightarrow{k} D$$

the over-all rate constant is the product $\underline{kK}$. Since from thermodynamics

$$K = \exp(-\Delta H/RT)\exp(\Delta S/R) \qquad (43)$$

and from transition state theory

$$k = (k_B T/h)\exp(-\Delta H^{\ddagger}/RT)\exp(\Delta S^{\ddagger}/R) \qquad (44)$$

it follows that

$$kK = (k_B T/h)\exp[-(\Delta H + \Delta H^{\ddagger})/RT]\exp[(\Delta S + \Delta S^{\ddagger})/R] \qquad (45).$$

That is, the over-all rate constant $\underline{kK}$ exhibits the same type of temperature dependence as a specific rate constant except that the calculated entropy of activation is now the sum of the $\Delta\underline{S}$ for the equilibrium and the $\Delta\underline{S}^{\ddagger}$ for the slow step. This conclusion can easily be extended to cases in which the over-all rate constants involve the product and/or quotient of two or more equilibrium constants.

The over-all rate constant, $\underline{k}_{II}$, is thus the sum of three terms, each of which follows Arrhenius temperature dependence. However, because of the mathematical properties of exponential functions, Arrhenius temperature will be observed for $\underline{k}_{II}$ only if the activation energies for the three terms are nearly the same and/or only one term contributes significantly to $\underline{k}_{II}$ (101). Thus, the fact that Arrhenius temperature dependence is observed for cerium(IV) oxidations in sulfuric acid media implies that the activation energies for the reactions with the three cerium(IV)-sulfate species are similar, and/or the partition is such that reaction with a single species predominates. The latter possibility may be most important, since it was shown in a previous section that the $CeSO_4^{2+}$ complex accounts for a major portion of the cerium(IV) oxidation reaction.

The energies and entropies of activation calculated for cerium(IV) oxidation reactions are thus over-all values which reflect the combined effects of several

factors. The values would be expected to vary, for example, with the nature of the reaction medium. Little significance should therefore be attached to the absolute magnitudes of these numbers. However, it is possible to compare the values obtained for related compounds in a single reaction medium since the contributions of the medium will be constant. Thus, as shown in Table XIV, while the absolute values of the entropies and energies of activation for cis- and trans-1,2-cyclopentanediols vary considerably with the nature of the reaction medium, the relative values remain nearly the same. The energies of activation for the two isomers are essentially the same and the entropies of activation are slightly more positive for the trans-isomer in all these media.

TABLE XIV

EFFECT OF REACTION MEDIUM ON ACTIVATION DATA FOR cis- AND trans-1,2-CYCLOPENTANEDIOLS

Reaction Medium	E_a		$\Delta S^{\ddagger}$	
	cis	trans	cis	trans
0.25M Sulfuric and 0.75M perchloric acids	23.3	23.2	14.7	15.4
0.75M Sulfuric and 0.25M perchloric acids	22.8	22.8	10.0	10.8
0.5M Sulfuric acid[a]	21.7	21.8	6.2	7.6

[a]Data from Reference (102).

Interpretation of the Activation Data

The most striking feature of the activation data given in Table XIII is that the differences in the energies and entropies of activation are relatively small. The activation energies for the diols and 2-methoxyalcohols are closely related to ring size. Thus, the activation energies for trans-2-methoxycyclopentanol and cis- and trans-1,2-cyclopentanediols vary only from 23.0 to 23.3 kcal. $mole^{-1}$. Also, the values for the 2-methoxycyclohexanols and 1,2-cyclohexanediols differ

only slightly (28.0 to 30.7). The fact that in both the five- and six-membered ring series the 2-methoxyalcohols give approximately the same activation energy as the 1,2-diols is consistent with the results of product analysis which showed that both are oxidized by carbon-carbon bond cleavage. Cyclopentanol, for which the rate-determining process involves carbon-hydrogen bond fission, gives an activation energy which is 4 kcal. mole^{-1} higher than the 1,2-oxygenated cyclopentane derivatives.

The difference of 5-7 kcal. mole^{-1} in the activation energies for the 1,2-oxygenated cyclopentane and cyclohexane derivatives probably reflects the greater internal strain in the cyclopentane ring. Because of the lower activation energy for the cyclopentane derivatives, these compounds react from 200 to 1000 times faster at 30°C. than the corresponding cyclohexane derivatives.

The entropies of activation calculated for the cyclohexane derivatives are consistent with the mechanisms indicated by the equilibrium constants determined in 1.0M perchloric acid. The results in 1.0M perchloric acid indicated that cis- and trans-1,2-cyclohexanediols were oxidized through a chelate complex. The chelate complex was shown to be a more rigid structure with the trans-isomer than with the cis. If the mechanism of oxidation of these compounds in sulfuric acid media also involves a cyclic intermediate, a more negative entropy of activation would be expected for the trans-isomer. On the other hand, if the reactions proceed via an acyclic intermediate the entropies of activation for the two isomers would be expected to be nearly the same. The significantly more negative entropy of activation observed for the trans-isomer (16.6 versus 23.0 cal. deg.$^{-1}$ mole^{-1} for the cis)* is thus additional evidence for reaction of the 1,2-cyclohexanediols by a cyclic mechanism.

*For comparison, the values of the entropy of activation in lead tetraacetate oxidation of cis- and trans-1,2-cyclohexanediols are 12.7 and 10.0 cal. deg.$^{-1}$ mole^{-1} [calculated from values of the Arrhenius frequency factor given by Criegee, et al. (45)].

The equilibrium constant obtained for trans-2-methoxycyclohexanol in 1.0M perchloric acid suggested that this compound forms an acyclic complex with cerium-(IV). The entropies of activation for the cis- and trans-2-methoxycyclohexanols (22.8 and 25.8 cal. deg.$^{-1}$ mole^{-1}, respectively) are also consistent with the acyclic mechanism for these compounds. If a cyclic intermediate were involved, the entropy of activation would be expected to be more negative for the trans-isomer. However, the value for the cis-isomer was found to be slightly more negative than for the trans. The substitution of a methyl group for an alcohol hydrogen thus effectively blocks chelation with cerium(IV).

The entropies of activation obtained for the cis- and trans-1,2-cyclopentanediols and trans-2-methoxycyclopentanol are practically identical. This result suggests that these compounds are oxidized via a common acyclic reaction mechanism, although the possibility of a chelate intermediate cannot be rigorously excluded for cis-1,2-cyclopentanediol. It is possible that this compound could react by a different mechanism than the trans-diol and trans-2-methoxycyclopentanol and still give about the same values for the entropy of activation. For example, approximately the same entropies of activation were found for cis-1,2-cyclohexanediol and cis-2-methoxycyclohexanol although the cerium(IV) complexes with these compounds are apparently different. The absence of any difference in the entropies of activation for the cis- and trans-1,2-cyclopentanediols does seem to exclude cyclic complex formation for the trans-isomer. Using scale models and assuming an octahedral cerium(IV) complex with 2.4 A. Ce-O bond lengths it was found that because of the long Ce-O bonds, chelated complexes could be formed with both the cis- and trans-1,2-cyclopentanediols. In both models the chelate ring is nonplanar and involves considerable angle strain. As in the 1,2-cyclohexanediols, the fused ring system formed with the trans-diol is somewhat less flexible than with the cis. While the differences between the model

chelates with the cis- and trans-diols are not very large, it has already been suggested that these models may not accurately represent the real situation, possibly because of errors in the assumed Ce-O bond length or cerium(IV) coordination number. The equilibrium constant data for the 1,2-cyclohexanediols indicates that the chelate rings assume a somewhat more planar conformation than predicted by the models. In this case, then, the differences between cis- and trans-isomers would be accentuated in the 1,2-cyclopentanediols, and formation of chelate would be difficult for the trans-isomer.

The inability to obtain values for the equilibrium constants for the reactions of the 1,2-cyclopentanediols makes it difficult to present definite conclusions concerning the nature of the cerium(IV)-substrate interaction. It is not possible to determine whether the interaction occurs as the transition state of a direct bimolecular oxidation reaction or if a coordination complex is formed, but only in small amounts. The latter possibility, however, seems most reasonable in the absence of definite evidence to the contrary. Since the methoxyl group in the 2-methoxycyclohexanols apparently does not coordinate with cerium(IV) to form a chelate complex, it is likely that trans-2-methoxycyclopentanol also reacts via an acyclic intermediate. While the thermodynamic data indicate an acyclic mechanism for the reaction of trans-1,2-cyclopentanediol, no definite conclusions can be drawn concerning the nature of the intermediate in the cerium(IV) oxidation of the cis-diol.

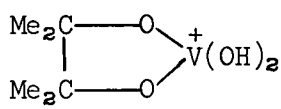
COMPARISON OF CERIUM(IV) AND OTHER OXIDANTS

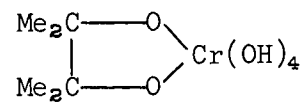
Cerium(IV) is one of many oxidants capable of oxidizing alcohols and glycols. While there are many similarities in the reaction mechanisms of the various oxidants, there are certain characteristic differences between oxidant types. In this section the reactions of cerium(IV) and some of the more familiar oxidants will be compared.

In its reactions with glycols, cerium(IV) resembles the two-electron oxidants lead tetraacetate and periodate ion. Thus, the results of this work with 1,2-cyclopentanediols and 1,2-cyclohexanediols, and previous studies with pinacol (5), 2,3-butanediol (3, 4), and ethylene glycol (47) indicate that cerium(IV) oxidizes glycols by carbon-carbon bond cleavage. On the other hand, chromium(VI) and vanadium(V) oxidize 2,3-butanediol by secondary alcohol oxidation ($>$CHOH $\rightarrow$ $>$C=O) to form acetoin, although ditertiary 1,2-glycols are necessarily oxidized by carbon-carbon bond cleavage (16).

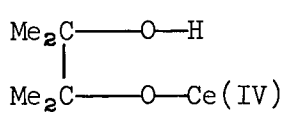
In contrast to lead tetraacetate and periodate ion, which are reasonably specific oxidants for 1,2-glycols, cerium(IV) can oxidize, in addition to glycols, alcohols, α-hydroxy acids, and carbonyl compounds. In these reactions, cerium(IV) resembles many oxidants including cobalt(III), manganese(III), and vanadium(V). The reactions of cerium(IV) with alcohols are somewhat slower than with 1,2-glycols, although the differences are not very great.

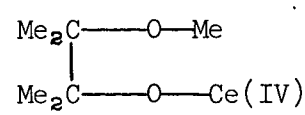
The oxidations of pinacol and pinacol monomethyl ether by cerium(IV), vanadium(V), and chromium(VI) have been compared by Littler and Waters (16). Vanadium (V) and chromium(VI) oxidize pinacol considerably faster than pinacol monomethyl ether, indicating that cyclic intermediates are formed in the oxidations of pinacol:



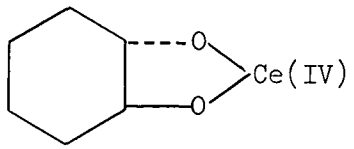


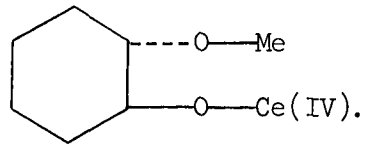
The rates of oxidation of pinacol and its monomethyl ether by cerium(IV) differed only slightly and a common acyclic intermediate was suggested





It was shown in this work that trans-1,2-cyclohexanediol forms a chelate intermediate with cerium(IV) whereas its monomethyl ether does not:

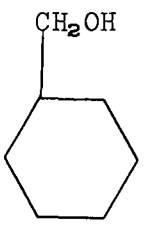




However, these compounds are oxidized by cerium(IV) at about the same over-all rate. It seems possible that the situation in the cerium(IV) oxidation of pinacol and its monomethyl ether may be similar. Thus, the significant difference between cerium(IV) and chromium(VI) and vanadium(V) is probably not in the nature of the complex formed with the glycol but rather that cerium(IV) is able to oxidize 2-methoxyalcohols via acyclic mechanisms at rates comparable to the oxidation of the glycols.

OXIDATIONS OF CELLULOSE MODEL COMPOUNDS

It was suggested in the Introduction that in cerium(IV) initiated graft polymerizations onto cellulose the most likely sites for the oxidation reaction are the C_2-C_3 glycol group and the C_6 hydroxyl of the anhydroglucose monomer unit. The reaction of trans-1,2-cyclohexanediol, which may be considered as a model for the C_2-C_3 glycol moiety, has already been discussed in some detail. This compound is apparently oxidized by disproportionation of a chelate complex to the dialdehyde adipaldehyde. The oxidations of cyclohexanemethanol (I) and tetrahydropyran-2-methanol (II) were studied as models for the C_6 hydroxyl. In Table XV the rates



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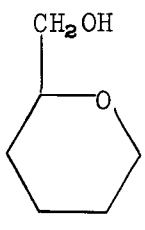

II

of oxidation of these compounds and trans-1,2-cyclohexanediol are compared. Although the oxidation products were not determined for these compounds it seems likely that the corresponding aldehydes would be formed since the primary alcohols, methanol and ethanol, yield formaldehyde (27) and acetaldehyde (29), respectively.

TABLE XV

OXIDATIONS OF CELLULOSE MODEL COMPOUNDS IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 30°C.

Substrate	Relative Rate
trans-1,2-Cyclohexanediol	6.0
Cyclohexanemethanol	1.3
Tetrahydropyran-2-methanol	1.0

While the extension of results obtained with model compounds to the reaction with the cellulose polymer involves certain difficulties, the relative rate data in Table XV suggest that the C_2-C_3 glycol unit would be oxidized more readily by cerium(IV) than the C_6 hydroxyl. However, the difference in the oxidation rates of the model compounds is not sufficiently large to totally exclude reaction at the primary hydroxyl. While the ring oxygen in tetrahydropyran-2-methanol apparently has little effect on the reaction at the C_6 hydroxyl it is possible that the C_4 and C_1 linkages in the cellulose molecule will affect the relative reactivities of the C_6 hydroxyl and the C_2-C_3 glycol. Furthermore, it is probable that changes in the reaction media will also affect the relative reactivities. Despite these complicating factors it seems reasonable to predict that, in the ceric ion oxidation of cellulose, reaction will occur primarily at the glycol unit and to some extent at the C_6 hydroxyl.

CONCLUSIONS

The oxidations of cis- and trans-1,2-cyclohexanediols by cerium(IV) proceed via chelate complex intermediates. Evidence was obtained for cyclic intermediates in these reactions from determinations of the equilibrium constants for complex formation in 1.0M perchloric acid and from thermodynamic activation data in 0.25M sulfuric and 0.75M perchloric acids. The nature of the interaction of cerium(IV) with cis- and trans-1,2-cyclopentanediols is less certain since these reactions could not be studied under conditions permitting determination of the equilibrium constant for complex formation. However, the entropies of activation for these compounds suggested that the trans-diol is oxidized via an acyclic mechanism.

Substitution of a methyl group for a hydroxyl hydrogen apparently prevents chelate complex formation with cerium(IV). However, trans-1,2-cyclohexanediol and trans-2-methoxycyclohexanol are oxidized by cerium(IV) at approximately the same rate, although the complex formed with these compounds is different. Thus, the nature of the complexes formed in cerium(IV) oxidations cannot be determined from measurements of relative rates of oxidation.

For reaction media containing from 0.25M to 0.75M sulfuric acid the cerium-(IV)-sulfate complexes $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$ participate in the oxidation reaction. The reactivities of the various species increase as the number of sulfate ions in the complex decreases, and in the range of sulfate ion concentrations studied the $CeSO_4^{2+}$ species accounts for a major portion of the reaction.

The relative reactivities of certain cellulose model compounds suggest that in the cerium(IV) initiated graft polymerization onto cellulose, the oxidation reaction of cerium(IV) with cellulose will occur mainly at the C_2-C_3 glycol unit and to a lesser extent at the C_6 primary hydroxyl.

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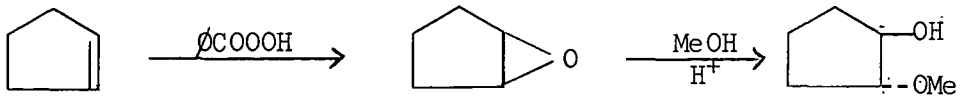
APPENDIX I

DETAILS OF COMPOUND PREPARATIONS

trans-2-METHOXYCYCLOPENTANOL



trans-2-Methoxycyclopentanol was prepared from cyclopentene by the reactions shown above. The peroxybenzoic acid was prepared either from benzoyl peroxide (103) or from benzoyl chloride and sodium peroxide (104). Cyclopentene (17.5 g., 0.26 mole) was added to a solution of 0.27 mole peroxybenzoic acid in 1 liter of chloroform. After 30 hr. at 0°C. the chloroform solution was washed with 10% sodium hydroxide (300 ml.) and water, dried (sodium sulfate) and the chloroform distilled off through a 20-cm. vigreux column. The cyclopentene oxide residue was then converted to trans-2-methoxycyclopentanol by a procedure analogous to a literature preparation of trans-2-methoxycyclohexanol (71). Methanol (200 ml.) and 4 drops of concentrated sulfuric acid were added to the cyclopentene oxide and the mixture refluxed for 4 hr. The cooled solution was neutralized with barium carbonate, filtered, and the methanol distilled off. The yield for the reaction based on cyclopentene was approximately 65%.

2-METHOXYCYCLOHEXANONE

2-Methoxycyclohexanone was prepared by oxidation of trans-2-methoxycyclohexanol with dichromate in acetic acid. The procedure used was adopted from an analogous preparation of cyclohexanone from cyclohexanol given by Fieser (76). The preparation of 2-methoxycyclohexanone by CrO_3 oxidation of trans-2-methoxycyclohexanol has been reported previously (77).

Sodium dichromate dihydrate (15 g., 0.05 mole) was dissolved in 25 ml. of acetic acid with heating and the solution cooled to 15°C. The dichromate solution was added to a cooled (15°C.) mixture of trans-2-methoxycyclohexanol (19.6 g., 0.15 mole) and 10 ml. of acetic acid. The temperature was allowed to rise to 60°C. and was maintained there by intermittent cooling in an ice bath until further cooling was unnecessary. After the reaction had cooled to room temperature, 100 ml. of water were added to the green solution and the product steam distilled. The distillate was almost clear and it was not certain if the ketone was being distilled. After 250 ml. of distillate had been collected the distillation was stopped. The distillate was extracted with ether, and the ether extract was washed with 10% sodium hydroxide and saturated sodium chloride solutions. The ether extract was dried with sodium sulfate and concentrated. Yield, 12.1 g. Similar extraction of the steam distillation residue yielded 3.4 g. The products were combined and fractionally distilled, b.p. 83-84°C. at 23 mm. [lit. b.p. 76°C. at 15 mm. (85)]. Semicarbazone m.p. 172-174°C. [lit. m.p. 178-179°C. (85)].

An infrared spectrum of the purified reaction product had a significant hydroxyl absorption band and examination of the product by gas chromatography showed considerable (ca. 25%) unreacted starting material. However, since this ketone was used only in the preparation of a reference 2,4-dinitrophenylhydrazone for qualitative product analysis, no further purification was carried out.

GLUTARALDEHYDE BIS(cis-1,2-CYCLOPENTANEDIOL ACETAL)

In product analysis work a crystalline precipitate was isolated from cis-1,2-cyclopentanediol and cerium(IV) reaction solutions and also from known cis-1,2-cyclopentanediol and glutaraldehyde solutions. This material was prepared in larger quantities for characterization by the following procedure.

cis-1,2-Cyclopentanediol (3.6 g., 0.035 mole) was dissolved in 1.0N sulfuric acid (100 ml.) and 2.0 ml. (0.005 mole) of 25% aqueous glutaraldehyde (Aldrich Chemical Co.) were added. The reaction solution became cloudy almost immediately. The mixture was put in a refrigerator for 48 hr. after which the crystalline product was filtered off, washed with water, and dried in a vacuum desiccator over Drierite. Yield, 1.2 g. (0.0045 mole, 90%).

The product was purified by dissolving the crystals in a small amount of 95% ethanol, filtering the solution and adding water dropwise until the solution became cloudy. The solution was then placed in a refrigerator overnight to crystallize. The crystals were then filtered off, washed with water and air dried. The product was recrystallized twice by this method, m.p. 43.7-44.3°C.

The purified product was dried over P_2O_5 at 34.6°C. (refluxing ethyl ether) and aspirator pressure. A sample of this material was submitted to Geller Microanalytical Laboratories for carbon and hydrogen analysis and molecular weight determination, mol. wt. 271; C 67.39%, H 8.92% (calcd. for $C_{15}H_{24}O_4$: mol. wt. 268.4; C 67.14%, H 9.01%).

APPENDIX II

CALCULATION OF INITIAL RATES

The occurrence of autocatalytic effects in many reactions in 0.25M sulfuric and 0.75M perchloric acids and the reaction of cyclohexanol in 1.0M perchloric acid necessitated the development of a procedure for calculation of initial rates. It was assumed that the primary oxidation reaction obeys second-order kinetics:

$$- dCe(IV)/dt = k_{II}SCe(IV) \qquad (46)$$

where

Ce(IV) = total cerium(IV)

S = substrate concentration

k_{II} = second-order rate constant.

Since the absorbance, A, is proportional to the total cerium(IV)

$$-dA/dt = k_{II}SA \qquad (47)$$

and

$$- d\ln A/dt = k_{II}S \qquad (48).$$

Because of the autocatalysis, $d\ln A/dt$ is not a constant as indicated by the above equation and it is necessary to evaluate this quantity at zero time:

$$\text{initial pseudo-first-order rate constant} = - (d\ln A/dt)_{t=0} = k_{II}S \qquad (49).$$

Two unsuccessful attempts were made to evaluate this quantity by analytic procedures. First, it was assumed that

$$\ln A = b_o + b_1 t + b_2 t^2 \qquad (50)$$

where b_o, b_1, and b_2 are regression coefficients. The regression coefficients were determined by a least squares technique using data restricted to the first

10 to 20% of the reaction and the initial rate calculated from the equation

$$-\left(d\ln A/dt\right)_{t=0} = -b_1 \qquad (51).$$

It was found that while the quadratic equation fit the data points quite well, the calculated initial rate did not agree well with graphical estimates. In a second attempt, a cubic term was added to the equation for ln A. The initial rates calculated from the cubic equation were better, but still did not seem to give a good estimate of the slope of the linear portion of the ln A versus time curve in all cases. The problem in these procedures seems to be an extreme sensitivity of the calculation to slight scatter in the ln A versus time plots at very early reaction times.

Because of the lack of success with the analytic calculations, initial rates were estimated simply by drawing a straight line through the initial linear portion of the ln A versus time plot. In Fig. 21 the data for a reaction of trans-1,2-cyclohexanediol in 0.25M sulfuric and 0.75M perchloric acids are shown together with analytic and visual estimates of the initial slope. The reaction shown here was chosen to illustrate a case in which particularly poor agreement between the various methods was obtained. In many instances the visual estimates and the results using the cubic equation for ln A were essentially the same.

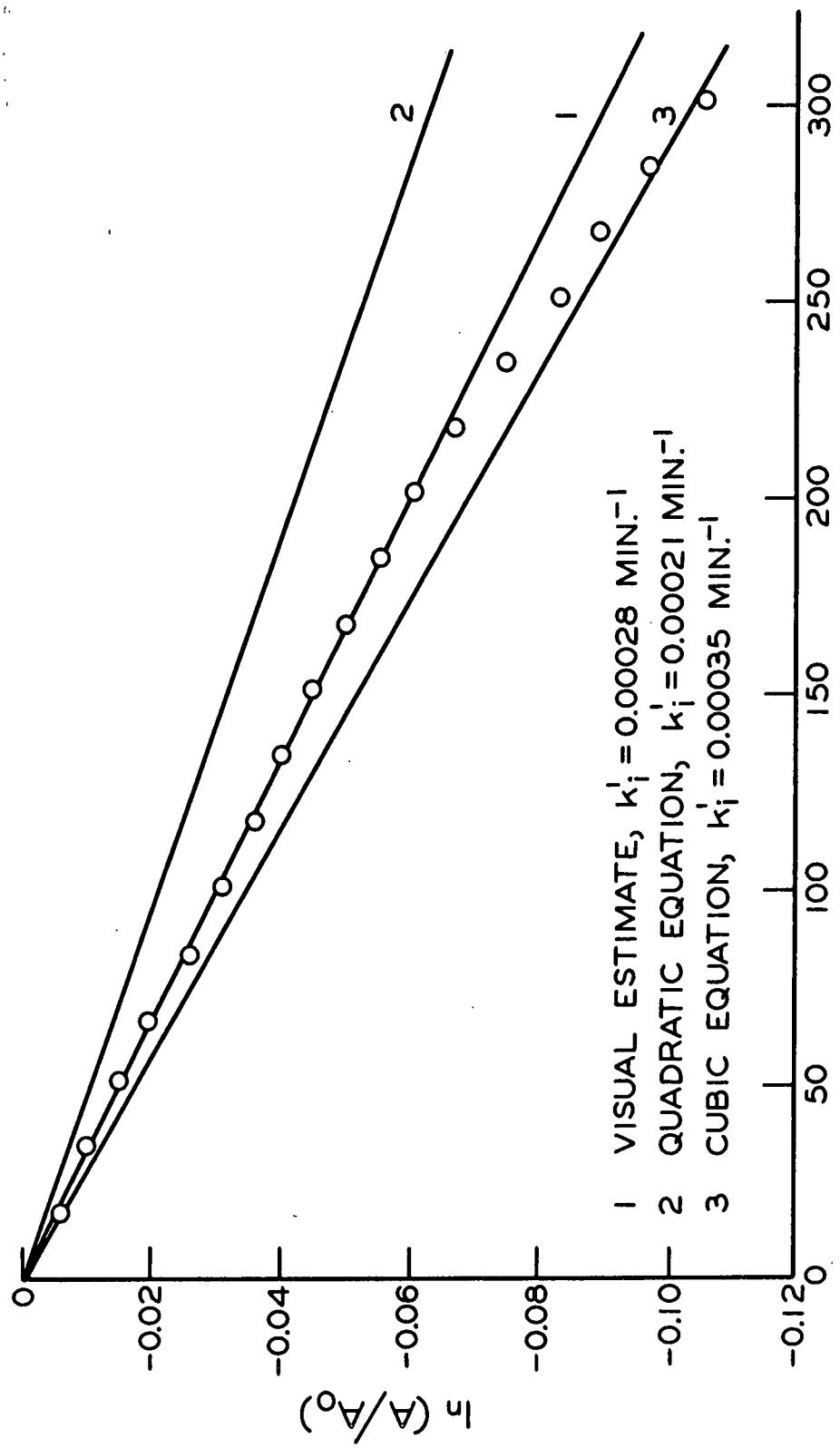


Figure 21. Determination of Initial Rate Constant for the Reaction of 0.040M trans-1,2-Cyclohexanediol in 0.25M Sulfuric and 0.75M Perchloric Acids at 20.0°C. Initial Cerium(IV) Concentration, 0.001M

APPENDIX III

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS

In this appendix the results of the product analysis and kinetic experiments are given along with the details of the experimental conditions (Tables XVI to LVIII). The original data for the kinetic experiments, which consisted of 20 to 30 pairs of time-absorbance values, are given for several typical reactions (corresponding to the experiments shown in Fig. 3 to 6 and 21). For the remainder of the kinetic experiments only the derived rate constants are presented. The kinetic experiments are identified by numbers which refer to the Research Notebook number, page, and run number.

PRODUCT ANALYSIS EXPERIMENTS

TABLE XVI

QUANTITATIVE DETERMINATION OF KNOWN CARBONYL COMPOUNDS
AS 2,4-DINITROPHENYLHYDRAZONES

Substrate	Concentrations, M			Weight of 2,4-DNPH, g.	Millimoles		Yield, %
	Substrate	H_2SO_4	$HClO_4$		Taken[a]	Found	
Adipaldehyde	0.00552	--	1.0	0.113	0.248	0.238	96.0
Cyclohexanone	0.00515	--	1.0	0.0666	0.255	0.2385	92.4
	0.00515	--	1.0	0.659	0.255	0.2360	91.5
Cyclopentanone	0.00489	0.25	0.75	0.0602	0.244	0.2270	93.0
	0.00489	0.25	0.75	0.0599	0.244	0.2259	92.6
Glutaraldehyde	0.00625	--	--	0.1177	0.250	0.2557	102.3
	0.00625	--	--	0.1165	0.250	0.2531	101.2
Glutaraldehyde[b]	0.0075	--	--	0.1216	0.2625	0.2642	100.6

[a]Calculated from molarity of substrate and volume of sample used in the determination.
[b]Determination in the presence of 0.1M trans-1,2-cyclopentanediol.

TABLE XVII

QUANTITATIVE DETERMINATION OF CARBONYL REACTION PRODUCTS AS 2,4-DINITROPHENYLHYDRAZONES

Substrate	Concentrations, M				Wt. of 2,4-DNPH, g.	Millimoles[a]		Yield, %
	Substrate	H_2SO_4	$HClO_4$	Ce(IV)		Expected	Found	
Cyclohexanol	0.1	--	1.0	0.00936	0.0453	0.234	0.162	69.3[b]
	0.1	--	1.0	0.00936	0.0472	0.234	0.169	72.3[b]
	0.1	--	1.0	0.01028	0.046	0.232	0.165	71
Cyclopentanol	0.1	--	1.0	0.01028	0.055	0.232	0.207	89.5
	0.1	0.25	0.75	0.00974	0.0295	0.195	0.111	57.1[b]
	0.1	0.25	0.75	0.00974	0.0283	0.195	0.107	54.8[b]
cis-1,2-Cyclohexanediol	0.1	--	1.0	0.00936	0.1093	0.234	0.230	98.5[b]
	0.1	--	1.0	0.00936	0.1093	0.234	0.230	98.5[b]
	0.1	--	1.0	0.01028	0.095	0.232	0.200	86.4
trans-1,2-Cyclohexanediol	0.1	--	1.0	0.00936	0.0997	0.234	0.210	89.8[b]
	0.1	--	1.0	0.00936	0.1013	0.234	0.214	91.3[b]
	0.1	--	1.0	0.01028	0.090	0.232	0.190	81.9
	0.1	0.25	0.75	0.00974	0.0225	0.195	0.047	24.3[b]
	0.1	0.25	0.75	0.00974	0.0256	0.195	0.054	27.7[b]
	3.7	0.25	0.75	0.00487	0.0389	0.122	0.082	67.4[b]

[a]Millimoles expected calculated from molarity of cerium(IV) and volume of sample used in the determination assuming two moles of cerium(IV) produce one mole of product. Millimoles found based on primary reaction product as given in Table VI.

[b]Reactants nitrogen purged before mixing.

TABLE XVII (Continued)

QUANTITATIVE DETERMINATION OF CARBONYL REACTION PRODUCTS AS 2,4-DINITROPHENYLHYDRAZONES

Substrate	Concentrations, M				Wt. of 2,4-DNPH, g.	Millimoles[a]		Yield, %
	Substrate	H_2SO_4	$HClO_4$	Ce(IV)		Expected	Found	
trans-2-Methoxycyclohexanol	0.1	--	1.0	0.00936	0.0608	0.234	0.128	54.8[b]
	0.1	--	1.0	0.00936	0.0612	0.234	0.129	55.1[b]
	0.1	--	1.0	0.01028	0.055	0.232	0.116	50.0
	0.1	0.25	0.75	0.00812	0.0200	0.243	0.042	17.4[b]
cis-2-Methoxycyclohexanol	0.1	0.25	0.75	0.00974	0.0230	0.243	0.048	24.9[b]
trans-1,2-Cyclopentanediol	0.1	0.25	0.75	0.00974	0.1156	0.243	0.251	103.3[b]
	0.1	0.25	0.75	0.00974	0.1153	0.243	0.250	103.1[b]
	0.1	0.25	0.75	0.0100	0.102	0.225	0.222	98.5
	0.1	0.5	--	0.015	0.1226	0.262	0.267	101.6
	0.1	0.5	--	0.015	0.1219	0.262	0.265	100.8
trans-2-Methoxycyclopentanol	0.1	0.25	0.75	0.00974	0.1169	0.243	0.254	104.5[b]
	0.1	0.25	0.75	0.00974	0.1176	0.243	0.256	105.2[b]
	0.1	0.25	0.75	0.0100	0.102	0.225	0.222	98.5

[a]Millimoles expected calculated from molarity of cerium(IV) and volume of sample used in the determination assuming two moles of cerium(IV) produce one mole of product. Millimoles found based on primary reaction product as given in Table VI.

[b]Reactants nitrogen purged before mixing.

TABLE XVIII

THIN-LAYER CHROMATOGRAPHY OF 2,4-DINITROPHENYLHYDRAZONES

2,4-Dinitrophenylhydrazone of	R_f[a] Benzene-Pet. Ether[b]	R_f[a] Benzene-Ethyl Acetate[b]
Adipaldehyde	0.02	0.34
1,2-Cyclohexanedione[c]	0.03 0.13	0.43 0.56
Cyclohexanone	0.32	0.64
Cyclopentanone	0.26	0.62
Glutaraldehyde	0.02	0.23
Formaldehyde	0.35	0.57
2-Methoxycyclohexanone[c]	0.14 0.30	0.52 0.60

[a]Typical R_f values. Values varied slightly with individual plates.

[b]95% Benzene.

[c]The two spots found with 1,2-cyclohexanedione and 2-methoxycyclohexanone may represent the *syn* and *anti* geometric isomers.

TYPICAL KINETIC EXPERIMENTS

TABLE XIX

REACTION OF 0.040*M* *cis*-1,2-CYCLOPENTANEDIOL IN 0.25*M* SULFURIC AND 0.75*M* PERCHLORIC ACIDS AT 15.0°C.[a]

t, min.	*A*	ln (*A*/*A*$_o$)	*t*, min.	*A*	ln (*A*/*A*$_o$)
1.25	1.067	-0.176	8.33	0.380	-1.209
1.66	1.002	-0.239	9.16	0.338	-1.326
2.08	0.941	-0.302	10.00	0.300	-1.445
2.50	0.887	-0.361	10.83	0.263	-1.577
2.91	0.833	-0.424	11.66	0.234	-1.694
3.33	0.783	-0.486	12.50	0.208	-1.811
3.75	0.739	-0.544	13.33	0.186	-1.923
4.16	0.695	-0.605	14.16	0.167	-2.031
5.00	0.617	-0.724	15.00	0.148	-2.152
5.83	0.546	-0.846	15.83	0.132	-2.266
6.66	0.483	-0.969	16.66	0.118	-2.378
7.50	0.429	-1.087	17.50	0.103	-2.514

[a]Experiment Number 2317-65-2. *A*$_o$ = 1.273. Data plotted in Fig. 3.

TABLE XX

REACTION OF 0.041*M* *trans*-1,2-CYCLOPENTANEDIOL IN 0.25*M* SULFURIC AND 0.75*M* PERCHLORIC ACIDS AT 15.0°C.[a]

t, min.	*A*	ln (*A*/*A*$_o$)	*t*, min.	*A*	ln (*A*/*A*$_o$)
0.73	1.073	-0.182	4.73	0.383	-1.213
1.06	0.982	-0.271	5.06	0.356	-1.286
1.40	0.898	-0.361	5.40	0.327	-1.371
1.73	0.821	-0.450	5.73	0.302	-1.450
2.06	0.758	-0.530	6.06	0.277	-1.537
2.40	0.693	-0.620	6.40	0.253	-1.627
2.73	0.637	-0.704	6.73	0.233	-1.710
3.06	0.584	-0.791	7.06	0.217	-1.781
3.40	0.538	-0.873	7.40	0.199	-1.867
3.73	0.493	-0.960	7.73	0.183	-1.951
4.06	0.454	-1.043	8.06	0.169	-2.031
4.40	0.419	-1.123	8.40	0.157	-2.104

[a]Experiment Number 2317-65-12. A_o = 1.288. Data plotted in Fig. 3.

TABLE XXI

REACTION OF 0.038M trans-2-METHOXYCYCLOPENTANOL IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 15.0°C.[a]

t, min.	A	ln (A/A$_o$)	t, min.	A	ln (A/A$_o$)
0.83	1.216	-0.083	11.67	0.407	-1.178
1.67	1.117	-0.168	12.50	0.373	-1.265
2.50	1.023	-0.256	13.33	0.343	-1.349
3.33	0.943	-0.338	14.17	0.314	-1.437
4.17	0.867	-0.422	15.00	0.290	-1.517
5.00	0.798	-0.505	15.83	0.266	-1.603
5.83	0.732	-0.591	16.67	0.243	-1.694
6.67	0.673	-0.675	17.50	0.223	-1.780
7.50	0.619	-0.759	18.33	0.204	-1.869
8.33	0.568	-0.845	19.17	0.189	-1.945
9.17	0.522	-0.929	20.00	0.173	-2.033
10.00	0.480	-1.013	20.83	0.159	-2.118
10.83	0.442	-1.095			

[a]Experiment Number 2317-100-9. A$_o$ = 1.322. Data plotted in Fig. 3.

TABLE XXII

REACTION OF 0.040M cis-1,2-CYCLOHEXANEDIOL IN 1.0M PERCHLORIC ACID AT 15.0°C.[a]

t, min.	A	ln (A/A$_o$)	t, min.	A	ln (A/A$_o$)
0.66	0.874	-0.292	2.00	0.478	-0.896
0.83	0.808	-0.371	2.16	0.442	-0.974
1.00	0.747	-0.449	2.33	0.412	-1.044
1.16	0.692	-0.526	2.50	0.383	-1.117
1.33	0.642	-0.601	2.66	0.355	-1.193
1.50	0.596	-0.675	2.83	0.331	-1.263
1.66	0.553	-0.750	3.00	0.308	-1.335
1.83	0.513	-0.825	3.16	0.287	-1.406

[a]Experiment Number 2389-24-14. A$_o$ = 1.171. Data plotted in Fig. 4.

TABLE XXIII

REACTION OF 0.040M trans-1,2-CYCLOHEXANEDIOL IN 1.0M PERCHLORIC ACID AT 15.0°C.[a]

t, min.	A	ln (A/A$_o$)	t, min.	A	ln (A/A$_o$)
1.12	0.813	-0.161	5.62	0.407	-0.853
1.62	0.748	-0.244	6.12	0.377	-0.929
2.12	0.692	-0.322	6.66	0.350	-1.004
2.62	0.640	-0.400	7.12	0.324	-1.001
3.12	0.594	-0.475	7.62	0.301	-1.154
3.62	0.551	-0.550	8.12	0.281	-1.223
4.12	0.509	-0.629	8.77	0.260	-1.301
4.62	0.473	-0.702	9.28	0.237	-1.393
5.12	0.438	-0.779			

[a]Experiment Number 2389-24-13. A$_o$ = 0.955. Data plotted in Fig. 4.

TABLE XXIV

REACTION OF 0.040M *trans*-2-METHOXYCYCLOHEXANOL IN 1.0M PERCHLORIC ACID AT 15.0°C.[a]

t, min.	A	ln (A/A$_o$)	t, min.	A	ln (A/A$_o$)
0.66	0.352	-0.169	3.16	0.182	-0.828
0.83	0.335	-0.218	3.33	0.173	-0.879
1.00	0.320	-0.264	3.50	0.167	-0.914
1.16	0.307	-0.305	3.66	0.159	-0.963
1.33	0.293	-0.352	3.83	0.152	-1.003
1.50	0.280	-0.397	4.00	0.145	-1.056
1.66	0.268	-0.441	4.16	0.139	-1.098
1.83	0.256	-0.487	4.50	0.132	-1.149
2.00	0.244	-0.535	4.33	0.127	-1.188
2.16	0.235	-0.573	4.66	0.122	-1.228
2.33	0.226	-0.612	4.83	0.117	-1.270
2.50	0.216	-0.657	5.00	0.112	-1.314
2.66	0.207	-0.700	5.16	0.108	-1.350
2.83	0.198	-0.744	5.33	0.103	-1.398
3.00	0.190	-0.785			

[a]Experiment Number 2389-24-17. A$_o$ = 0.416. Data plotted in Fig. 4.

TABLE XXV

REACTION OF 0.040M cis-1,2-CYCLOHEXANEDIOL IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 20.0°C.[a]

t, min.	A	ln (A/A$_o$)	t, min.	A	ln (A/A$_o$)
9.2	0.908	-0.089	342.5	0.627	-0.459
42.5	0.885	-0.115	375.8	0.590	-0.519
75.8	0.863	-0.140	409.2	0.553	-0.585
109.2	0.841	-0.166	442.5	0.516	-0.654
142.5	0.816	-0.196	475.8	0.479	-0.727
175.8	0.788	-0.230	509.2	0.443	-0.807
209.2	0.760	-0.267	542.5	0.408	-0.889
242.5	0.730	-0.307	575.8	0.373	-0.979
275.8	0.696	-0.350	609.2	0.341	-1.068
309.2	0.662	-0.404	642.5	0.310	-1.164

[a]Experiment Number 2389-57-2. A$_o$ = 0.993. Data plotted in Fig. 5.

TABLE XXVI

REACTION OF 0.040*M* *trans*-1,2-CYCLOHEXANEDIOL IN 0.25*M* SULFURIC AND 0.75*M* PERCHLORIC ACIDS AT 20.0°C.[a]

t, min.	*A*	ln (*A*/*A*$_o$)	*t*, min.	*A*	ln (*A*/*A*$_o$)
9.2	0.909	-0.068	417.5	0.750	-0.259
42.5	0.903	-0.074	459.2	0.722	-0.298
84.2	0.893	-0.085	500.8	0.691	-0.342
125.8	0.883	-0.097	542.5	0.660	-0.388
167.5	0.872	-0.109	584.2	0.627	-0.439
209.2	0.859	-0.124	625.8	0.593	-0.495
250.8	0.841	-0.143	667.5	0.561	-0.549
292.5	0.822	-0.168	709.2	0.529	-0.609
334.2	0.802	-0.193	750.8	0.498	-0.669
375.8	0.778	-0.223			

[a]Experiment Number 2389-47-3. A_o = 0.973. Data plotted in Fig. 5.

TABLE XXVII

REACTION OF 0.039*M* *trans*-2-METHOXYCYCLOHEXANOL IN 0.25*M* SULFURIC AND 0.75*M* PERCHLORIC ACIDS AT 20.0°C.[a]

t, min.	*A*	ln (*A*/*A*$_o$)	*t*, min.	*A*	ln (*A*/*A*$_o$)
9.2	0.909	-0.026	342.5	0.821	-0.128
42.5	0.901	-0.034	375.8	0.810	-0.141
75.8	0.897	-0.039	409.2	0.798	-0.156
109.2	0.888	-0.049	442.5	0.783	-0.175
142.5	0.881	-0.057	475.8	0.769	-0.193
175.8	0.873	-0.066	509.2	0.753	-0.214
209.2	0.862	-0.078	542.5	0.739	-0.233
242.5	0.854	-0.088	575.8	0.722	-0.255
275.8	0.845	-0.099	609.2	0.707	-0.277
309.2	0.833	-0.113	642.5	0.690	-0.301

[a] Experiment Number 2389-60-1. A_o = 0.933. Data plotted in Fig. 5.

TABLE XXVIII

REACTION OF 0.16M CYCLOHEXANOL IN 1.0M PERCHLORIC ACID AT 15.0°C.[a]

t, min.	A	ln (A/A$_o$)	t, min.	A	ln (A/A$_o$)
1.67	0.800	-0.135	17.92	0.319	-1.055
2.92	0.757	-0.191	19.17	0.294	-1.136
4.17	0.712	-0.252	20.42	0.270	-1.222
5.42	0.670	-0.313	21.67	0.248	-1.307
6.67	0.627	-0.379	22.92	0.228	-1.391
7.92	0.588	-0.443	24.17	0.210	-1.473
9.17	0.548	-0.514	25.42	0.193	-1.557
10.42	0.510	-0.586	26.67	0.178	-1.638
11.67	0.474	-0.659	27.92	0.163	-1.726
12.92	0.440	-0.733	29.17	0.152	-1.796
14.17	0.408	-0.809	30.42	0.141	-1.871
15.42	0.377	-0.888	31.92	0.130	-1.952
16.67	0.348	-0.968	32.92	0.121	-2.024

[a]Experiment Number 2389-76-2. A$_o$ = 0.916. Data plotted in Fig. 6.

TABLE XXIX

REACTION OF 0.026M CYCLOHEXANOL IN 1.0M PERCHLORIC ACID AT 15.0°C.[a]

t, min.	A	ln (A/A$_o$)	t, min.	A	ln (A/A$_o$)
2.5	0.305	-0.067	69.2	0.149	-0.783
9.2	0.289	-0.121	75.5	0.139	-0.853
15.9	0.271	-0.185	82.5	0.130	-0.920
22.5	0.253	-0.254	89.2	0.123	-0.975
29.2	0.237	-0.319	95.9	0.113	-1.060
35.9	0.220	-0.394	102.5	0.100	-1.182
42.5	0.203	-0.474	109.2	0.080	-1.405
49.2	0.187	-0.556	115.9	0.070	-1.539
55.9	0.172	-0.640	122.5	0.063	-1.644
62.5	0.159	-0.718	129.2	0.057	-1.744

[a]Experiment Number 2389-85-4. A$_o$ = 0.326. Data plotted in Fig. 6.

TABLE XXX

REACTION OF 0.040M trans-1,2-CYCLOHEXANEDIOL IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 15.0°C.[a]

t, min.	A	ln (A/A$_o$)	t, min.	A	ln (A/A$_o$)
17.5	0.911	-0.006	167.5	0.871	-0.050
34.2	0.907	-0.010	184.2	0.867	-0.055
50.8	0.902	-0.015	200.8	0.862	-0.061
67.5	0.898	-0.020	217.5	0.857	-0.067
84.2	0.893	-0.026	234.2	0.850	-0.075
100.8	0.888	-0.031	250.8	0.843	-0.083
117.5	0.884	-0.036	267.5	0.838	-0.089
134.2	0.880	-0.040	284.2	0.831	-0.097
150.8	0.876	-0.045	300.8	0.823	-0.107

[a]Experiment Number 2389-47-1. A$_o$ = 0.916. Data plotted in Fig. 21.

RESULTS OF KINETIC EXPERIMENTS

TABLE XXXI

DETERMINATION OF MOLAR ABSORPTIVITY OF CERIUM(IV) IN 0.5M SULFURIC ACID AT 400 mμ AND 15.0°C.

Cerium(IV) Concn., M	Absorbance	Molar Absorptivity, M^{-1} $cm.^{-1}$
0.00200	1.866	933
0.00160	1.493	933
0.00100	0.933	933
0.00080	0.758	947
0.00050	0.463	926
0.00040	0.369	922
0.00025	0.229	916
0.00010	0.089	890

Molar absorptivity determined from a least squares regression of the absorbance versus the cerium(IV) concentration was 936 M^{-1} $cm.^{-1}$.

TABLE XXXII

REACTIONS OF cis-1,2-CYCLOPENTANEDIOL IN 0.5M SULFURIC ACID AT 14.8 TO 14.9°C.

Experiment Number	Initial Cerium(IV) Concn., M	Substrate Concn., M	λ, mμ	Temp., °C.	k', $min.^{-1}$
1. Reaction Rates Determined by Spectrophotometric Method					
2277-51	0.01	0.0428	450	14.8	0.0362
2277-52	0.01	0.0428	450	14.8	0.0365
2277-53	0.005	0.0428	440	14.8	0.0390
2277-57	0.001	0.0426	400	14.9	0.0406
2277-58	0.001	0.0426	400	14.9	0.0401
2277-58A	0.001	0.0852	400	14.9	0.0780
2277-59	0.001	0.0852	400	14.9	0.0808
2277-60	0.001	0.162	400	14.8	0.148
2277-62	0.001	0.121	400	14.8	0.112
2277-63	0.001	0.0996	400	14.8	0.0932
2277-64	0.001	0.154	400	14.8	0.141
2. Reaction Rates Determined by Titration Method					
2277-41	0.01	0.0400		14.9	0.0362
2277-42[a]	0.01	0.0400		14.9	0.0370
2277-47[b]	0.01	0.0400		14.9	0.0351
2277-44	0.01	0.100		14.9	0.0872
2277-46	0.01	0.160		14.9	0.150

[a]Reaction run in dark flask.
[b]Reaction run under nitrogen.

TABLE XXXIII

EFFECT OF THE INITIAL CERIUM(IV) CONCENTRATION FOR REACTIONS OF cis-1,2-CYCLOPENTANEDIOL IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 15.0°C.

Experiment Number	Substrate Concn., M	Initial Cerium(IV) Concn., M	λ, mμ	k', $min.^{-1}$
2317-61-4	0.0158	0.005	438	0.0528
2317-61-5	0.0163	0.005	438	0.0530
2317-63-11	0.0158	0.001	400	0.0574
2317-63-9	0.0163	0.001	400	0.0577
2317-60-1	0.0158	0.0005	380	0.0579
2317-60-4	0.0163	0.0005	380	0.0578
2317-63-5	0.0158	0.00025	317.5	0.0587
2317-63-1	0.0163	0.00025	317.5	0.0592

TABLE XXXIV

EFFECT OF THE INITIAL CERIUM(IV) CONCENTRATION FOR REACTIONS OF trans-1,2-CYCLOPENTANEDIOL IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 15.0°C.

Experiment Number	Substrate Concn., M	Initial Cerium(IV) Concn., M	λ, mμ	k', $min.^{-1}$
2317-63-8	0.0162	0.001	400	0.0969
2317-63-10	0.0164	0.001	400	0.0963
2317-61-1	0.0162	0.0005	380	0.0989
2317-60-5	0.0164	0.0005	380	0.0994
2317-63-3	0.0162	0.00025	317.5	0.0986
2317-63-4	0.0164	0.00025	313.5	0.0993

TABLE XXXV

EFFECT OF SUBSTRATE CONCENTRATION FOR REACTIONS OF cis-1,2-CYCLOPENTANEDIOL WITH 0.00025M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 15.0°C.

Experiment Number	Substrate Concn., M	k', $min.^{-1}$	k'/Substrate Concn., $min.^{-1}$ M^{-1}	Average
2317-63-5	0.0158	0.0587	3.71	
2317-63-1	0.0163	0.0592	3.63	3.67
2317-65-2	0.0396	0.145	3.65	
2317-65-7	0.0407	0.150	3.69	3.67
2317-65-3	0.0792	0.292	3.69	
2317-65-8	0.0814	0.292	3.59	3.64
2317-65-4	0.119	0.420	3.53	
2317-65-9	0.122	0.431	3.53	3.53
2317-65-6	0.158	0.547	3.46	
2317-65-10	0.163	0.573	3.52	3.49

TABLE XXXVI

EFFECT OF SUBSTRATE CONCENTRATION FOR REACTIONS OF trans-1,2-CYCLOPENTANEDIOL WITH 0.00025M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 15.0°C.

Experiment Number	Substrate Concn., M	k', $min.^{-1}$	k'/Substrate Concn., $min.^{-1}$ M^{-1}	Average
2317-63-4	0.0164	0.0993	6.05	
2317-63-3	0.0162	0.0986	6.09	6.07
2317-65-12	0.0410	0.255	6.22	
2317-65-17	0.0405	0.240	5.92	6.07
2317-65-13	0.0820	0.498	6.07	
2317-65-18	0.0810	0.491	6.06	6.06
2317-65-14	0.123	0.748	6.08	
2317-65-19	0.121	0.709	5.84	5.96
2317-65-15	0.164	0.929	5.66	
2317-65-20	0.162	0.952	5.88	5.77

TABLE XXXVII

EFFECT OF SUBSTRATE CONCENTRATION FOR REACTIONS OF trans-2-METHOXYCYCLOPENTANOL WITH 0.00025M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 15.0°C.

Experiment Number	Substrate Concn., M	k', $min.^{-1}$	k'/Substrate Concn., $min.^{-1}$ M^{-1}	Average
2317-100-8	0.0154	0.0428	2.78	
2317-100-7	0.0149	0.0416	2.79	2.78
2317-100-9	0.0380	0.101	2.67	
2317-100-10	0.0371	0.0996	2.69	2.68
2317-100-11	0.0760	0.194	2.56	
2317-100-12	0.0742	0.192	2.59	2.58
2317-100-13	0.114	0.281	2.46	
2317-100-14	0.111	0.274	2.47	2.46
2317-100-15	0.152	0.363	2.39	
2317-100-16	0.148	0.357	2.40	2.40

TABLE XXXVIII

EFFECT OF SUBSTRATE CONCENTRATION FOR REACTIONS OF cis-1,2-CYCLOPENTANEDIOL WITH 0.001M CERIUM(IV) IN 0.5M SULFURIC ACID AT 15.0°C.

Experiment Number	Substrate Concn., M	k', $min.^{-1}$	k'/Substrate Concn., $min.^{-1}$ M^{-1}	Average
2277-113	0.0160	0.0165	1.031	
2277-112	0.0160	0.0158	0.988	1.010
2277-114	0.0400	0.0391	0.978	
2277-108	0.0400	0.0395	0.988	0.983
2277-115	0.0800	0.0761	0.951	
2277-110	0.0800	0.0767	0.959	0.955
2277-116	0.120	0.114	0.950	
2277-111	0.120	0.115	0.958	0.954
2277-117	0.160	0.148	0.925	
2277-109	0.160	0.149	0.931	0.928

TABLE XXXIX

EFFECT OF SUBSTRATE CONCENTRATION FOR REACTIONS OF trans-1,2-CYCLOPENTANEDIOL WITH 0.001M CERIUM(IV) IN 0.5M SULFURIC ACID AT 15.0°C.

Experiment Number	Substrate Concn., M	k', $min.^{-1}$	k'/Substrate Concn., $min.^{-1}$ M^{-1}	Average
2277-104	0.0161	0.0235	1.46	
2277-95	0.0160	0.0237	1.48	1.47
2277-103	0.0402	0.0586	1.46	
2277-92	0.0400	0.0594	1.48	1.47
2277-102	0.0803	0.118	1.47	
2277-94	0.0800	0.115	1.44	1.46
2277-101	0.120	0.175	1.46	
2277-93	0.120	0.173	1.44	1.45
2277-100	0.161	0.229	1.42	
2277-91	0.160	0.230	1.44	1.43

TABLE XL

REACTIONS OF *cis*-1,2-CYCLOHEXANEDIOL WITH 0.0025*M* CERIUM(IV) IN 1.0*M* PERCHLORIC ACID

Experiment Number	Substrate Concn., *M*	Temp., °C.	*k'*, $min.^{-1}$	$A_o - A_b$
2389-29-13	0.0160	10.0	0.112	0.593
2389-29-14	0.0160	10.0	0.113	0.536
2389-29-2	0.0320	10.0	0.171	0.909
2389-29-3	0.0320	10.0	0.169	1.027
2389-23-3	0.0160	15.0	0.262	--
2389-24-3	0.0160	15.0	0.256	0.595
2389-37-1	0.0160	15.0	0.256	0.562
2389-24-7	0.0240	15.0	0.339	0.764
2389-24-8	0.0240	15.0	0.340	0.733
2389-24-14	0.0400	15.0	0.448	1.018
2389-24-15	0.0400	15.0	0.470	1.008
2389-24-28	0.0801	15.0	0.601	1.302
2389-24-29	0.0800	15.0	0.607	1.271
2389-24-22	0.160	15.0	0.644	1.532
2389-24-23	0.160	15.0	0.669	1.558
2389-35-11	0.0160	20.0	0.556	0.544
2389-35-12	0.0160	20.0	0.543	0.569
2389-35-4	0.0320	20.0	0.920	0.839
2389-35-5	0.0320	20.0	0.901	0.842

TABLE XLI

REACTIONS OF *trans*-1,2-CYCLOHEXANEDIOL WITH 0.0025*M* CERIUM(IV) IN 1.0*M* PERCHLORIC ACID

Experiment Number	Substrate Concn., *M*	Temp., °C.	*k'*, $min.^{-1}$	$A_o - A_b$
2389-29-9	0.0160	10.0	0.0339	0.434
2389-29-10	0.0161	10.0	0.0330	0.464
2389-29-6	0.0320	10.0	0.0524	0.741
2389-29-7	0.0321	10.0	0.0528	0.728
2389-23-2	0.0160	15.0	0.0804	0.442
2389-24-4	0.0161	15.0	0.0796	0.422
2389-24-5	0.0240	15.0	0.104	0.593
2389-24-6	0.0241	15.0	0.104	0.607
2389-24-12	0.0401	15.0	0.151	0.825
2389-24-13	0.0402	15.0	0.152	0.800
2389-24-26	0.0801	15.0	0.211	1.146
2389-24-27	0.0804	15.0	0.211	1.121
2389-24-18	0.160	15.0	0.274	1.494
2389-24-19	0.161	15.0	0.275	1.453
2389-35-9	0.0160	20.0	0.175	0.423
2389-35-10	0.0161	20.0	0.172	0.429
2389-35-2	0.0320	20.0	0.287	0.700
2389-35-3	0.0321	20.0	0.281	0.687

TABLE XLII

REACTIONS OF *trans*-2-METHOXYCYCLOHEXANOL WITH 0.0025*M* CERIUM(IV) IN 1.0*M* PERCHLORIC ACID

Experiment Number	Substrate Concn., *M*	Temp., °C.	*k'*, $min.^{-1}$	$A_o - A_b$
2389-29-11	0.0161	10.0	0.0455	0.110
2389-29-12	0.0160	10.0	0.0443	0.111
2389-29-4	0.0322	10.0	0.0960	0.206
2389-29-5	0.0320	10.0	0.0917	0.201
2389-23-4	0.0161	15.0	0.112	--
2389-24-2	0.0160	15.0	0.107	0.114
2389-37-3	0.0160	15.0	0.111	0.100
2389-37-4	0.0241	15.0	0.162	0.153
2389-24-10	0.0240	15.0	0.164	0.158
2389-24-16	0.0402	15.0	0.261	0.259
2389-24-17	0.0400	15.0	0.263	0.263
2389-24-30	0.0805	15.0	0.505	0.473
2389-24-31	0.0801	15.0	0.490	0.447
2389-24-24	0.161	15.0	0.838	0.713
2389-24-25	0.160	15.0	0.810	0.712
2389-35-13	0.0161	20.0	0.241	0.115
2389-35-14	0.0160	20.0	0.239	0.113
2389-35-6	0.0322	20.0	0.470	0.211
2389-35-7	0.0320	20.0	0.442	0.219

TABLE XLIII

REACTIONS OF CYCLOHEXANOL WITH 0.0025M CERIUM(IV) IN 1.0M PERCHLORIC ACID

Experiment Number	Substrate Concn., M	Temp., °C.	k_i', $min.^{-1}$	$A_o - A_b$
2389-79-3	0.0241	10.0	0.00417	0.133
2389-79-4	0.0239	10.0	0.00347	0.156
2389-79-1	0.0481	10.0	0.00748	0.293
2389-79-2	0.0478	10.0	0.00812	0.294
2389-85-3	0.0241	15.0	0.00862	0.153
2389-85-4	0.0239	15.0	0.00864	0.161
2389-85-6	0.0359	15.0	0.0130	0.225
2389-85-1	0.0481	15.0	0.0143	0.287
2389-85-2	0.0478	15.0	0.0158	0.290
2389-76-3	0.0802	15.0	0.0244	0.431
2389-76-4	0.0797	15.0	0.0255	0.432
2389-76-1	0.160	15.0	0.0461	0.713
2389-76-2	0.160	15.0	0.0453	0.710
2389-80-1	0.0241	20.0	0.0172	0.152
2389-81-1	0.0239	20.0	0.0171	0.147
2389-81-2	0.0478	20.0	0.0347	0.273
2389-81-3	0.0481	20.0	0.0353	0.275

TABLE XLIV

EFFECT OF SULFATE ION CONCENTRATION FOR REACTIONS OF cis-1,2-CYCLOPENTANEDIOL WITH 0.00025M CERIUM(IV) AT 15.0°C.

Experiment Number	Substrate Concn., M	H_2SO_4 Concn., M	$HClO_4$ Concn., M	k', $min.^{-1}$
2317-63-5	0.0158	0.25	0.75	0.0587
2317-63-1	0.0163	0.25	0.75	0.0592
2317-75-2	0.0159	0.35	0.65	0.0344
2317-75-3	0.0163	0.35	0.65	0.0358
2317-75-7	0.0159	0.45	0.55	0.0241
2317-75-8	0.0163	0.45	0.55	0.0248
2317-75-12	0.0159	0.55	0.45	0.0183
2317-75-13	0.0163	0.55	0.45	0.0188
2317-75-17	0.0159	0.65	0.35	0.0146
2317-75-18	0.0163	0.65	0.35	0.0149
2317-75-22	0.0159	0.75	0.25	0.0121
2317-75-23	0.0163	0.75	0.25	0.0124

TABLE XLV

EFFECT OF SULFATE ION CONCENTRATION FOR REACTIONS OF trans-1,2-CYCLOPENTANEDIOL WITH 0.00025M CERIUM(IV) AT 15.0°C.

Experiment Number	Substrate Concn., M	H_2SO_4 Concn., M	$HClO_4$ Concn., M	k', $min.^{-1}$
2317-63-3	0.0162	0.25	0.75	0.0986
2317-63-4	0.0164	0.25	0.75	0.0993
2317-75-5	0.0162	0.35	0.65	0.0581
2317-75-4	0.0164	0.35	0.65	0.0580
2317-75-10	0.0162	0.45	0.55	0.0394
2317-75-9	0.0164	0.45	0.55	0.0398
2317-75-15	0.0162	0.55	0.45	0.0297
2317-75-14	0.0164	0.55	0.45	0.0300
2317-75-20	0.0162	0.65	0.35	0.0234
2317-75-19	0.0164	0.65	0.35	0.0234
2317-75-25	0.0162	0.75	0.25	0.0194
2317-75-24	0.0164	0.75	0.25	0.0196

TABLE XLVI

TEMPERATURE DEPENDENCE OF REACTIONS OF cis-1,2-CYCLOPENTANEDIOL WITH 0.00025M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k', $min.^{-1}$	k'/Substrate Concn., $min.^{-1}$ M^{-1}
2317-91-9	0.0163	10.0	0.0289	1.77
2389-34-1	0.0160	10.0	0.0292	1.84
2317-63-5	0.0158	15.0	0.0587	3.71
2317-63-1	0.0163	15.0	0.0592	3.63
2317-86-1	0.0159	20.0	0.118	7.44
2317-86-2	0.0163	20.0	0.120	7.38
2317-92-1	0.00396	30.0	0.110	27.8
2317-92-2	0.00407	30.0	0.112	27.6

TABLE XLVII

TEMPERATURE DEPENDENCE OF REACTIONS OF trans-1,2-CYCLOPENTANEDIOL WITH 0.00025M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k', $min.^{-1}$	k'/Substrate Concn., $min.^{-1}$ M^{-1}
2317-91-10	0.0164	10.0	0.0472	2.88
2317-91-11	0.0162	10.0	0.0468	2.89
2317-63-4	0.0164	15.0	0.0993	6.05
2317-63-3	0.0162	15.0	0.0986	6.09
2317-86-3	0.0164	20.0	0.196	11.97
2317-86-4	0.0162	20.0	0.190	11.77
2317-92-3	0.00404	30.0	0.181	44.6
2317-92-4	0.00404	30.0	0.179	44.2

TABLE XLVIII

TEMPERATURE DEPENDENCE OF REACTIONS OF trans-2-METHOXYCYCLOPENTANOL WITH 0.00025M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k', $min.^{-1}$	k'/Substrate Concn., $min.^{-1}$ M^{-1}
2317-100-2	0.0154	10.0	0.0211	1.37
2317-100-1	0.0149	10.0	0.0206	1.38
2317-100-8	0.0154	15.0	0.0428	2.78
2317-100-7	0.0149	15.0	0.0416	2.79
2317-100-5	0.0154	20.0	0.0846	5.50
2317-100-6	0.0149	20.0	0.0828	5.56
2317-100-4	0.0154	30.0	0.309	20.1
2317-100-3	0.0149	30.0	0.306	20.5

TABLE XLIX

TEMPERATURE DEPENDENCE OF REACTIONS OF cis-1,2-CYCLOPENTANEDIOL WITH 0.00025M CERIUM(IV) IN 0.75M SULFURIC AND 0.25M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k', $min.^{-1}$	k'/Substrate Concn., $min.^{-1}$ M^{-1}
2317-91-6	0.0163	10.0	0.00623	0.382
2389-78-1	0.0160	10.0	0.00619	0.387
2317-75-22	0.0159	15.0	0.0121	0.764
2317-75-23	0.0163	15.0	0.0124	0.760
2317-91-1	0.0119	20.0	0.0181	1.52
2317-91-2	0.0122	20.0	0.0187	1.53
2317-92-5	0.00793	30.0	0.0444	5.60
2317-92-8	0.00815	30.0	0.0451	5.53

TABLE L

TEMPERATURE DEPENDENCE OF REACTIONS OF trans-1,2-CYCLOPENTANEDIOL WITH 0.00025M CERIUM(IV) IN 0.75M SULFURIC AND 0.25M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k', $min.^{-1}$	k'/Substrate Concn., $min.^{-1}$ M^{-1}
2317-91-7	0.0164	10.0	0.00977	0.596
2317-91-8	0.0162	10.0	0.00970	0.600
2317-75-24	0.0164	15.0	0.0196	1.20
2317-75-25	0.0162	15.0	0.0194	1.20
2317-91-3	0.0123	20.0	0.0292	2.38
2317-91-4	0.0121	20.0	0.0290	2.39
2317-92-6	0.00819	30.0	0.0708	8.64
2317-92-7	0.00809	30.0	0.0702	8.68

TABLE LI

REACTIONS OF cis-1,2-CYCLOHEXANEDIOL WITH 0.001M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k_i', $min.^{-1}$	k_i'/Substrate Concn., $min.^{-1}$ M^{-1}
2389-57-1	0.0392	20.0	0.000743	0.0190
2389-57-2	0.0396	20.0	0.000731	0.0184
2389-68-2	0.0389	30.0	0.00391	0.100
2389-114-4	0.0395	30.0	0.00450	0.114
2389-74-2	0.0396	40.0	0.0182	0.460
2389-74-3	0.0389	40.0	0.0178	0.456

TABLE LII

REACTIONS OF trans-1,2-CYCLOHEXANEDIOL WITH 0.001M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k_i', $min.^{-1}$	k_i'/Substrate Concn., $min.^{-1}$ M^{-1}
2389-47-1	0.0398	20.0	0.000281	0.00706[a]
2389-47-3	0.0398	20.0	0.000230	0.00578
2389-50-2	0.0390	20.0	0.000257	0.00644
2389-50-1	0.0390	20.0	0.000251	0.00629[a]
2389-65-1	0.0398	30.0	0.00126	0.0316
2389-66-1	0.0399	30.0	0.00128	0.0322
2389-73-3	0.0390	40.0	0.00552	0.138
2389-73-4	0.0390	40.0	0.00535	0.134

[a]Reactant purged 30 minutes with nitrogen before mixing.

TABLE LIII

REACTIONS OF cis-2-METHOXYCYCLOHEXANOL WITH 0.001M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k_i', $min.^{-1}$	k_i'/Substrate Concn., M^{-1} $min.^{-1}$
2389-92-1	0.0381	20.0	0.00109	0.0285
2389-92-2	0.0389	20.0	0.00106	0.0271
2389-114-1	0.0382	30.0	0.00544	0.142
2389-114-2	0.0389	30.0	0.00523	0.134
2389-113-1	0.0382	40.0	0.0256	0.670
2389-113-2	0.0389	40.0	0.0257	0.660

TABLE LIV

REACTIONS OF trans-2-METHOXYCYCLOHEXANOL WITH 0.001M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k_i', $min.^{-1}$	k_i'/Substrate Concn., M^{-1} $min.^{-1}$
2389-60-1	0.0386	20.0	0.000220	0.00569
2389-60-3	0.0387	20.0	0.000250	0.00647
2389-68-1	0.0387	30.0	0.00137	0.0354
2389-69-1	0.0387	30.0	0.00140	0.0363
2389-74-1	0.0387	40.0	0.00696	0.180
2389-74-4	0.0386	40.0	0.00660	0.171

TABLE LV

REACTIONS OF CYCLOHEXANOL WITH 0.001M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k_i', $min.^{-1}$	k_i'/Substrate Concn., M^{-1} $min.^{-1}$
2389-50-3	0.0771	20.0	0.000429	0.00556
2389-50-4	0.0766	20.0	0.000299	0.00390
2389-65-2	0.0771	30.0	0.001242	0.01611
2389-67-2	0.0766	30.0	0.000711	0.00928
2389-73-1	0.0771	40.0	0.00198	0.0157
2389-73-2	0.0766	40.0	0.00182	0.0238

TABLE LVI

REACTIONS OF CYCLOPENTANOL WITH 0.001M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS

Experiment Number	Substrate Concn., M	Temp., °C.	k_i', $min.^{-1}$	k_i'/Substrate Concn., M^{-1} $min.^{-1}$
2389-54-1	0.0389	20.0	0.000525	0.0135
2389-54-2	0.0382	20.0	0.000526	0.0138
2389-66-2	0.0388	30.0	0.00282	0.0726
2389-67-1	0.0381	30.0	0.00251	0.0660
2389-73-6	0.0388	40.0	0.0108	0.278
2389-73-7	0.0382	40.0	0.0106	0.276

TABLE LVII

REACTIONS OF CYCLOHEXANEMETHANOL AND TETRAHYDROPYRAN-2-METHANOL WITH 0.001M CERIUM(IV) IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 30.0°C.

Experiment Number	Substrate	Substrate Concn., M	k', $min.^{-1}$
2389-114-3	Tetrahydropyran-2-methanol	0.0303	0.000167
2389-71-1		0.0351	0.000182
2389-71-2	Cyclohexanemethanol	0.0304	0.000202
2389-69-2		0.0316	0.000216

TABLE LVIII

EFFECT OF NITROGEN PURGING ON REACTIONS IN 0.25M SULFURIC AND 0.75M PERCHLORIC ACIDS AT 20°C.

Experiment Number	Substrate Concn., M	Nitrogen Purged	k', $min.^{-1}$
1. cis-1,2-Cyclopentanediol			
2389-63-1	0.0200	No	0.1169
2389-63-4	0.0200	No	0.1178
2389-63-2	0.0200	Yes	0.1195
2389-63-3	0.0200	Yes	0.1190
2. trans-1,2-Cyclopentanediol			
2389-63-6	0.0206	No	0.1987
2389-63-9	0.0206	No	0.1970
2389-63-7	0.0206	Yes	0.2014
2389-63-8	0.0206	Yes	0.2028
3. trans-1,2-Cyclohexanediol			
2389-47-3	0.0398	No	0.000230
2389-50-1	0.0390	No	0.000251
2389-47-1	0.0398	Yes	0.000281
2389-50-2	0.0390	Yes	0.000257